

Anal. Calcd for $C_{20}H_{16}O_4$: C, 75.0; H, 5.0. Found: C, 75.0; H, 5.0.

3-Deoxysericetin (16) and 3-Deoxyisericetin (15). To a solution of **2** (500 mg) in dry benzene (40 ml) was added DDQ (300 mg) and the whole solution refluxed for 1 hr. It was filtered while hot, benzene distilled off, and the residue subjected to column chromatography. Elution with benzene–light petroleum (2:8) gave a solid which again proved to be a mixture. Fractional crystallization with light petroleum (mother liquor A) yielded the sparingly soluble solid which on recrystallization from ethyl acetate–light petroleum mixture afforded 5-hydroxy-6-prenyl-6'',6''-dimethylpyrano[2'',3'':7,8]flavone [3-deoxyisericetin (15)] (120 mg): mp 156°; R_f 0.78 (solvent A); light green ferric reaction; nmr δ 1.50 [s, 6, $(CH_3)_2C<$], 1.70, 1.83 [2 broad s, 6, $(CH_3)_2C=$], 3.41 (d, 2, $J = 7$ Hz, $ArCH_2$), 5.33 (m, 1, $-CH=$), 5.67 6.88 (2 d, 2, $J = 10$ Hz, two olefinic H of pyran ring), 6.70 (s, 1 H in position 3), 7.59 (m, 3 H in positions 3', 4', and 5') and 7.93 (m, 2 H in positions 2' and 6'); mass spectrum (70 eV) m/e (rel intensity) 388 (85), 373 (100), 345 (57), 332 (63), 317 (11), 215 (17), 165 (11), 105 (11), 77 (10).

Anal. Calcd for $C_{25}H_{24}O_4$: C, 77.3; H, 6.2. Found: C, 76.8; H, 5.9.

The mother liquor A yielded a solid which after crystallization twice from methanol yielded 5-hydroxy-8-prenyl-6'',6''-dimethylpyrano[2'',3'':7,6]flavone [3-deoxysericetin (16)] (80 mg) as pale yellow needles: mp 166°; R_f 0.74 (solvent A); intense green ferric reaction; nmr δ 1.50 [s, 6, $(CH_3)_2C<$], 1.72, 1.79 [2d, 6, $J = 2$ Hz, $(CH_3)_2C=$], 3.56 (d, 2, $J = 7$ Hz, $ArCH_2$), 5.26 (m, 1, $-CH=$), 5.66, 6.81 (2 d, 2, $J = 10$ Hz, two olefinic H of pyran ring), 6.71 (s, 1 H in position 3), 7.59 (m, 3 H in positions 3', 4', and 5'), and 7.96 (m, 2 H in positions 2' and 6'); mass spectrum (70 eV) m/e (rel intensity) 388 (82), 373 (100), 345 (68), 333 (73), 215 (28), 165 (14), 105 (27), 85 (36), 77 (22), 71 (55), 55 (46).

Anal. Calcd for $C_{25}H_{24}O_4$: C, 77.3; H, 6.2. Found: C, 76.8; H, 5.9.

Acknowledgment. One of us (B. N. S.) thanks UGC, India, for a fellowship.

Registry No.—1, 480-40-0; 2, 50678-89-2; 2 diacetate, 50678-90-5; 3, 50678-91-6; 3 diacetate, 50678-92-7; 4, 50678-93-8; 5, 50678-94-9; 6, 50678-95-0; 7, 50678-96-1; 8, 50830-97-2; 9, 50678-97-2; 10, 34187-26-3; 11, 34125-75-2; 11 diacetate, 50678-98-3; 12, 50678-99-4; 13, 50679-00-0; 14, 34187-25-2; 15, 50679-01-1; 16,

50679-02-2; prenyl bromide, 870-63-3; 2-hydroxy-2-methyl-3-butene, 115-18-4.

References and Notes

- (1) Correspondence should be addressed to Department of Chemistry, Himachal University, The Manse Building, Simla-1,71,001, India.
- (2) K. Venkataraman, *Phytochem.*, **11**, 157 (1972).
- (3) P. V. Radha Krishnan, A. V. Rama Rao, and K. Venkataraman, *Tetrahedron Lett.*, 663 (1965).
- (4) P. C. Parthasarthy, P. V. Radha Krishnan, S. S. Rathi, and K. Venkataraman, *Indian J. Chem.*, **7**, 101 (1969), and earlier papers in this series.
- (5) K. G. Dave, R. Mani, and K. Venkataraman, *J. Sci. Ind. Res., Sect. B*, **20**, 112 (1961).
- (6) K. G. Dave, S. A. Telang, and K. Venkataraman, *Tetrahedron Lett.*, 9 (1962).
- (7) A. V. Rama Rao, M. Vardan, and K. Venkataraman, *Indian J. Chem.*, **9**, 7 (1971).
- (8) A. V. Rama Rao, S. S. Rathi, and K. Venkataraman, *Indian J. Chem.*, **10**, 905, 989 (1972).
- (9) V. H. Deshpande, P. C. Parthasarthy, and K. Venkataraman, *Tetrahedron Lett.*, 1715 (1968).
- (10) M. M. Pashchenko, G. P. Pivnenko, and V. I. Litvinenko, *Formatsevt, Zh. Kiev.*, **21** (1), 44 (1966).
- (11) M. M. Pashchenko and G. P. Pivnenko, *Formatsevt, Zh. Kiev.*, **21** (5), 47 (1966).
- (12) K. N. N. Ayengar, B. Y. Rama Sastry, and S. Rangaswami, *Indian J. Chem.*, **11**, 85 (1973).
- (13) A. C. Jain, S. K. Mathur, and T. R. Seshadri, *J. Sci. Ind. Res. Sect. B*, **21**, 214 (1962).
- (14) J. Hlubucek, E. Ritchie, and W. C. Taylor, *Aust. J. Chem.*, **24**, 2348 (1971).
- (15) B. F. Burrows, W. D. Ollis, and L. M. Jackman, *Proc. Chem. Soc.*, 177 (1960).
- (16) A. V. Rama Rao, M. Varadan, and K. Venkataraman, *Indian J. Chem.*, **9**, 7 (1971).
- (17) All melting points were taken on Buchi melting point apparatus and are uncorrected. Tlc was carried out on plates coated with silica gel supplied by NCL, Poona. Spraying reagent was generally 10% aqueous sulfuric acid, but 10% alcoholic ferric chloride was also used for such compounds which gave positive ferric reaction. Tlc was carried out using one of the following solvent systems: (A) benzene, (B) benzene–ethyl acetate (9:1), (C) benzene–ethyl acetate (75:25), (D) benzene–ethyl acetate (1:1). Column chromatography was carried out using silica gel supplied by NCL, Poona. Nuclear magnetic resonance spectra were determined in $CDCl_3$ using 60 MHz spectrophotometer. Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane as internal standard. Mass spectra were determined on samples introduced through the heated inlet system using MS 72 spectrometer, 70 eV ionizing voltage, 900×10 trap current, and 2.0 kV accelerating voltage.

1,8 Interactions in Naphthalene Derivatives. An X-Ray Structure Determination and Nuclear Magnetic Resonance Studies of 1,8-Di(bromomethyl)naphthalene¹

J.-B. Robert,² J. S. Sherfinski, Richard E. Marsh, and John D. Roberts*

Contribution No. 4790 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109

Received November 13, 1973

The conformation of 1,8-di(bromomethyl)naphthalene has been determined in the crystalline state and it has been found that the molecule has essentially twofold symmetry about the C-9–C-10 bond with the bromines located above and below the plane of the ring. The carbon–bromine bonds are inclined toward one another about 10° from planes perpendicular to the naphthalene ring which contain the C-1–C-11 and C-8–C-12 bonds. This conformation has formally nonbonded H...Br distances of 2.85 Å which are substantially less than the sum of the van der Waals radii and could well indicate some degree of electrostatic binding. The strain in the molecule is largely relieved both by in-plane and out-of-plane bending of the C-1–C-11 and the C-8–C-12 bonds as well as some skeletal distortion of the ring. Low-temperature proton nmr studies of 1,8-di(bromomethyl)naphthalene and some related compounds showed no evidence of barriers to rotation about the C-1–C-11 and C-8–C-12 bonds large enough to be detectable.

Alkyl or aryl substituents at the 1,8 positions (the peri positions) of naphthalene are in close proximity to one another and provide many interesting opportunities for study of conformations and barriers to rotation about the extracyclic bonds, C-1–C-11 and C-8–C-12.^{3,4} Relatively few other simple molecules have the special feature of

having the substituents close to one another and attached to a relatively rigid framework by essentially parallel bonds. Because of the importance of knowing just what conformations are, in fact, favored for molecules of this type, we have determined the structure of 1,8-di(bromomethyl)naphthalene (1) by X-ray diffraction. On the as-

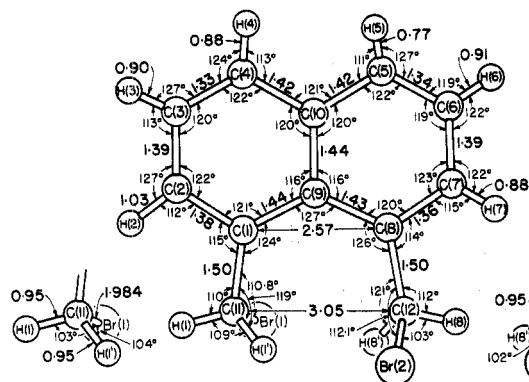
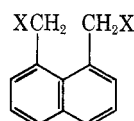


Figure 1. Bond angles and bond distances found for 1 in the crystal. Estimated standard deviations in the bond distances are about 0.006 Å for C-Br, 0.01 Å for C-C, and 0.06 Å for C-H.

sumption that the conformation observed for the solid state might also be important in solution, we have investigated the proton nmr spectra of 1 and of several related compounds (2-4) at low temperatures.

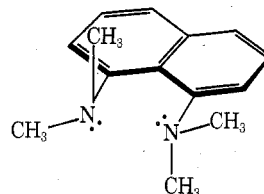


- 1, X = Br
- 2, X = H
- 3, X = Cl
- 4, X = OH

Most of the 1,8-disubstituted naphthalenes bearing substituents at the 1,8 positions whose structures have been investigated by X-ray diffraction have been halogen derivatives. These substances have no complications of extracyclic conformations but do show substantial nonplanarity, both of the halogens with respect to the rings and of the naphthalene rings themselves.⁵ Relief of steric strain is normally most easily achieved by bond bending, but for 1,8-disubstituted naphthalenes there is a buttressing effect exerted by the 2,7 hydrogens which tends to favor out-of-plane distortions. This type of interaction for dihalonaphthalenes reaches an extreme with 1,8-diiodonaphthalene.⁶

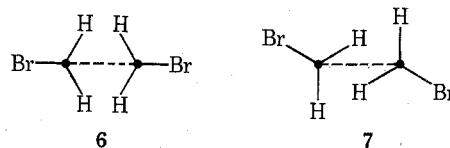
The crystallographic investigations of substances where conformational properties should be important include 3-bromo-1,8-dimethyl-⁷ and octamethylnaphthalenes,⁸ but in these two studies the methyl hydrogens were not located; 1,8-dinitronaphthalene,⁹ where the planes of the nitro groups are twisted about 43° from the plane of the ring; 1,4,5,8-tetranitronaphthalene¹⁰ with similar conformations of the nitro groups; 1,8-diphenylnaphthalene,^{4a} where the phenyl rings are face-to-face but substantially splayed outward and inclined to approximately 45° from the plane of the naphthalene ring; 1,4,5,8-tetraphenylnaphthalene,¹¹ which is similarly disposed; the conjugate acid of 1,8-bis(dimethylamino)naphthalene,¹² which has the added proton in the plane of the ring shared between the two nitrogen lone pairs; the methyl groups are above and below the

plane; and 1,8-bis(dimethylamino)naphthalene,¹³ the only case really comparable to the present one in that it involves saturated substituents. 1,8-Bis(dimethylamino)naphthalene assumes what appears to be a compromise conformation (5), with the methyl groups not in the most favorable location to avoid the hydrogens on C-2 and C-7, with the unshared pairs not face-to-face, and possibly with some degree of lone-pair delocalization in the ring (which, of course, would be particularly favored with the methyl groups in the plane of the ring).



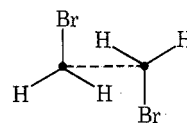
5

Some of the more symmetrical, possible conformations of 1 are 6-8, which represent end-on views at C-11 and C-12 and are chosen to avoid close proximity of bromines with the respective opposite carbons C-11 and C-12, or other obvious steric conflicts between substituents on these atoms. Of these, 6 would be expected to be the least favorable because of the eclipsing of the hydrogens and the interactions of the bromines with the hydrogens at C-2 and C-7. Arrangements 7 and 8 relieve these interactions at the cost of creating new nonbonded hydrogen-hydrogen (and, for 8, hydrogen-bromine) interactions. Clearly, the mode by which the molecule resolves these conflicts is of substantial interest.



6

7



8

Experimental Section

1,8-Di(bromomethyl)naphthalene (1) was prepared as described¹⁴ and recrystallized from ether. Preliminary Weissenberg and precession photographs indicated the monoclinic space group $C2/c$ (systematic absences: hkl for $(h+k)$ odd, $h0l$ for l odd). Unit-cell dimensions were derived from a least-squares fit to 20 values for 15 medium- to high-angle reflections centered on a diffractometer; they are $a = 23.500 \pm 0.004$ Å, $b = 7.662 \pm 0.002$ Å, $c = 12.543 \pm 0.006$ Å, $\beta = 95.73 \pm 0.02^\circ$.¹⁵ The density calculated for eight molecules in the unit cell is 1.856 g cm⁻³, in satisfactory agreement with the value 1.850 ± 0.002 g cm⁻³ measured by flotation.

The crystal used for collection of intensity data was an approximate cube, 0.2 mm on an edge, mounted along the c axis. Intensities were measured using a Daxex-automated General Electric three-circle diffractometer equipped with a copper-target X-ray tube, Ni filter, scintillation counter, and pulse-height analyzer.

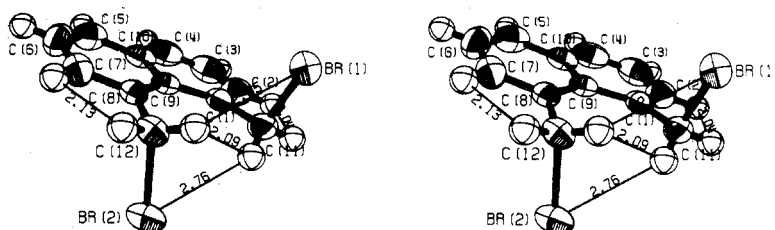


Figure 2. Stereoview of 1,8-di(bromomethyl)naphthalene (1) as it exists in the crystal.

Table I
Atomic Coordinates As Determined by
X-Ray Diffraction^a

	<i>x</i>	<i>y</i>	<i>z</i>
Br (1)	0.15221 (3)	-0.29088 (8)	0.00417 (5)
Br (2)	0.09420 (3)	0.16626 (9)	-0.24065 (5)
C (1)	0.1777 (2)	0.0748 (7)	0.0346 (4)
C (2)	0.2267 (3)	0.1128 (10)	0.1000 (5)
C (3)	0.2270 (4)	0.2348 (11)	0.1820 (6)
C (4)	0.1785 (4)	0.3152 (10)	0.2002 (5)
C (5)	0.0752 (4)	0.3690 (8)	0.1591 (5)
C (6)	0.0258 (3)	0.3454 (9)	0.0981 (6)
C (7)	0.0251 (3)	0.2396 (8)	0.0079 (5)
C (8)	0.0719 (2)	0.1498 (7)	-0.0182 (4)
C (9)	0.1251 (2)	0.1657 (6)	0.0470 (4)
C (10)	0.1261 (3)	0.2834 (7)	0.1365 (4)
C (11)	0.1838 (3)	-0.0682 (9)	-0.0452 (5)
C (12)	0.0623 (3)	0.0475 (8)	-0.1202 (4)
H (1)	0.223 (2)	-0.095 (7)	-0.048 (4)
H (1')	0.166 (2)	-0.055 (7)	-0.116 (4)
H (2)	0.261 (2)	0.039 (7)	0.081 (4)
H (3)	0.262 (2)	0.254 (7)	0.216 (4)
H (4)	0.176 (2)	0.396 (7)	0.250 (4)
H (5)	0.081 (2)	0.431 (7)	0.208 (4)
H (6)	-0.006 (2)	0.404 (7)	0.114 (4)
H (7)	-0.006 (2)	0.227 (7)	-0.037 (4)
H (8)	0.022 (2)	0.038 (7)	-0.145 (4)
H (8')	0.077 (2)	-0.067 (7)	-0.125 (4)

^a Values in parentheses are standard deviations in the last digit.

All reflections with $2\theta < 120^\circ$ were recorded using a θ - 2θ scan mode at a scan rate of 1° (in 2θ)/min; the scan width varied from 2.0° at $2\theta = 0^\circ$ to 2.9° at $2\theta = 120^\circ$. A 20-sec background count was recorded at each scan extremum. Three check reflections (10, 2, 2; 10, 0, 6; 0, 2, 4) were recorded periodically; they showed steady but somewhat unequal drops in intensity, averaging about 10% over the 5-day period. The recorded intensities were corrected for this average decay, and for Lorentz and polarization effects; no absorption corrections were applied ($\mu r \approx 1.0$). Assigned variances $\sigma^2(F_o^2)$ were based on counting statistics plus the term $(0.02S)^2$, where S is the scan count. Of the 1675 independent reflections that were recorded, 1551 had net intensities greater than zero.

The structure was derived by standard heavy-atom techniques beginning with a three-dimensional Patterson map.¹⁶ Two cycles of least-squares refinement of the heavy-atom coordinates (C and Br) gave an R value of 0.17. During the remaining eight least-squares cycles, additional parameters were added until they totaled 158: coordinates and anisotropic temperature factors for the 14 heavy atoms, coordinates for the 10 hydrogen atoms (which were initially assigned on geometric grounds), a scale factor, and a secondary-extinction parameter.¹⁷ The hydrogen atoms were assigned fixed, isotropic temperature factors with $B = 5.0 \text{ \AA}^2$. During the final refinement cycle, the largest shift in a heavy-atom parameter was 0.5σ and, in a hydrogen-atom coordinate,

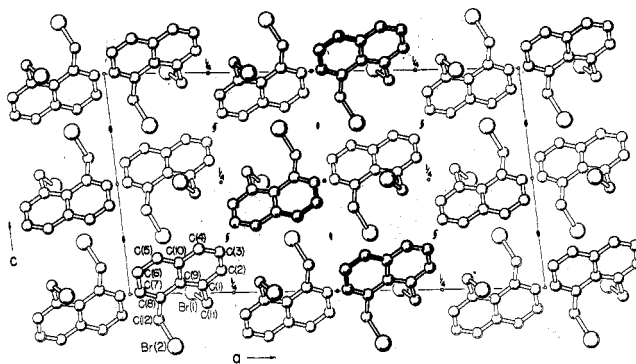


Figure 3. Arrangement of molecules of 1 in the crystal.

0.9σ . The goodness-of-fit, $[\sum w(F_o^2 - F_c^2)^2 / (N - P)]^{1/2}$ for $N = 1675$ reflections and $P = 158$ parameters, was 1.36; the R index, $\sum ||F_o| - |F_c|| / \sum |F_o|$, was 0.056 for the 1551 reflections with net intensities greater than zero.

Results and Discussion

The final atomic coordinates are given in Table I and the anisotropic temperature parameters in Table II. Bond distances and angles are shown in Figure 1, a stereoptic view of the molecule in Figure 2, and the arrangement of the molecules in Figure 3.

Bond distances in the naphthalene ring are in excellent agreement with values found in 1,8-bis(dimethylamino)naphthalene, the only other 1,8-disubstituted naphthalene derivative to have been studied with comparable accuracy. Once again we note that the four ring C-C bonds involving C-1 and C-8 are appreciably longer—by an average of 0.025 \AA in the present case—than the corresponding bonds involving C-4 and C-5. In the case of 1,8-bis(dimethylamino)naphthalene¹³ the effect was somewhat larger, 0.035 \AA , and was attributed in part to the electron-withdrawing ability of the substituent nitrogen atoms, and in part to overcrowding of the peri groups. In the present case, the substituent $-\text{CH}_2\text{Br}$ groups should have little electronic influence on the ring bonds, so that the distortion must be blamed almost entirely on overcrowding. A comparison of bond distances with those found for naphthalene¹⁸ and perdeuterionaphthalene¹⁹ suggests that this overcrowding leads to a redistribution of bonding electrons within the naphthalene nucleus, the bonds involving C-4 and C-5 being shortened by about the same amount that those involving C-1 and C-8 are lengthened.

Overcrowding between the peri $-\text{CH}_2\text{Br}$ groups is relieved in two additional ways: in-plane bending of the C-1-C-11 and C-8-C-12 bonds, and out-of-plane distortions involving the entire molecule. Deviations of the individual

Table II
Anisotropic Temperature Parameters^a

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br (1)	6.06 (4)	4.59 (3)	5.27 (4)	1.41 (3)	1.22 (3)	0.72 (3)
Br (2)	6.08 (4)	5.77 (4)	3.40 (3)	-0.16 (3)	0.02 (2)	1.24 (3)
C (1)	3.7 (3)	4.1 (3)	3.4 (2)	0.0 (2)	0.3 (2)	1.1 (2)
C (2)	4.2 (3)	6.9 (4)	4.5 (3)	0.2 (3)	-0.2 (3)	0.9 (3)
C (3)	5.5 (4)	7.3 (5)	5.0 (4)	-1.6 (4)	-1.4 (3)	1.4 (3)
C (4)	8.7 (5)	5.2 (4)	3.8 (3)	-2.0 (4)	0.0 (3)	0.0 (3)
C (5)	8.9 (5)	3.4 (3)	4.6 (3)	-0.2 (3)	2.3 (4)	-0.9 (2)
C (6)	5.6 (4)	4.7 (3)	7.3 (4)	1.1 (3)	2.4 (4)	0.4 (3)
C (7)	4.7 (3)	4.7 (3)	4.9 (4)	0.6 (3)	0.2 (3)	0.3 (3)
C (8)	4.2 (3)	3.1 (2)	3.3 (2)	0.1 (2)	0.7 (2)	0.8 (2)
C (9)	4.2 (3)	3.1 (2)	2.8 (2)	-0.5 (2)	0.5 (2)	0.7 (2)
C (10)	5.8 (3)	3.2 (3)	3.1 (3)	-0.9 (3)	0.4 (2)	0.4 (2)
C (11)	4.0 (3)	5.8 (3)	3.6 (3)	1.1 (3)	0.7 (2)	1.1 (3)
C (12)	4.1 (3)	3.9 (3)	3.5 (3)	-0.1 (2)	-0.3 (2)	0.5 (2)

^a Values in parentheses are standard deviations in the last digit. The temperature factors have the general form $\exp -\frac{1}{4}(B_{11}h^2a^{*2} + \dots + 2B_{23}hkb^*c^*)$.

Table III
Deviations from the Least-Squares Plane of the Naphthalene Ring^a

Atom	Deviation, Å	Atom	Deviation, Å
C (1)	-0.068	C (8)	0.051
C (2)	-0.020	C (7)	0.045
C (3)	0.047	C (6)	-0.041
C (4)	0.037	C (5)	-0.041
C (9)	0.000	C (10)	-0.010
C (11)	-0.229	C (12)	0.188
Br (1)	-2.110	Br (2)	2.024

^a The plane was passed through atoms C-1-C-10, all weighted equally. The direction cosines of the plane relative to *a*, *b*, and *c* are 0.2911, 0.7511, and -0.6186, and the origin-to-plane distance is 1.445 Å.

Table IV
Ring-Proton Coupling Constants and Chemical-Shift Differences for 1,8-Di(bromomethyl)naphthalene (1), 1,8-Dimethylnaphthalene (2), 1,8-Di(chloromethyl)naphthalene (3), and 1,8-Di(hydroxymethyl)naphthalene (4)

Compd	Solvent	J_{28} , Hz	J_{24} , Hz	J_{34} , Hz	δ_{43} , ppm	δ_{42} , ppm
1	CCl ₄	7.5	1.6	8.5	0.28	0.43
2	CCl ₄	7.0	1.8	7.4	0.38	0.42
3	CCl ₄	7.5	1.4	8.9	0.30	0.44
4	DMSO ^a	7.5	1.5	8.6	0.23	0.42

^a Dimethyl sulfoxide.

atoms from the mean plane of the naphthalene ring are given in Table III. These deviations are smaller than in the dimethylamino compound,¹³ while the in-plane splaying of the C-CH₂Br bonds is larger; presumably the double-bond character in the C-1-N and C-8-N bonds of the dimethylamino compound makes bond bending a less attractive mechanism for relieving strain than in the present case.

The puckering of the naphthalene system is accomplished primarily by a twist about the central C-9-C-10 bond by about 4° in the present compound and 9° in the dimethylamino compound. This twist apparently results in a redistribution of electrons in the ring system, for in both compounds (as well as in other peri compounds⁷⁻¹³ the C-9-C-10 bond is significantly longer than in naphthalene and perdeuterionaphthalene while the C-2-C-3 and C-6-C-7 bonds are marginally shorter.

The C-1-C-11 and C-8-C-12 bonds are sufficiently non-parallel as to result in a C-11...C-12 distance of 3.05 Å compared to 2.57 Å for C-1...C-8. This C-11...C-12 distance is substantially larger than the corresponding distance in 3-bromo-1,8-dimethylnaphthalene, 2.92 Å.⁷ The conformations about the C-CH₂Br bonds are such that the bromine atoms are directed to opposite sides of the molecular plane: the torsion angles C-2-C-1-C-11-Br-1 and C-7-C-8-C-12-Br-2 are 101.1 and 101.8°. A number of the nonbonded distances (Figure 2) are less than the sums of the van der Waals radii as given by Pauling²⁰ or Bondi.²¹ The most uncomfortable interactions appear to be the Br-1...H-8' (2.85 Å) and Br-2...H-1' (2.76 Å) contacts; however, it is possible that these interactions include electrostatic attraction effects of the type postulated to account for the unusual stability of axial halogens on cyclohexane rings in the presence of polar groups.²²

Nmr Studies. The arrangement and general tightness of the bromomethyl groups of 1 as shown in Figure 2 suggest that the hydrogens on the methylene groups should be nonequivalent and that there might be a significant barrier to rotation, a process which would, of course, make the methylene hydrogens on the average equivalent. For this reason, some variable-temperature nmr studies

were made of 1 and some related compounds, 2, 3, and 4. At room temperature, the proton interactions on the ring carbons of 1-4 were analyzed²³ as independent ABC spin systems on the assumption that the couplings between the hydrogens on opposite sides of the molecule were small, as they are in other naphthalene derivatives.²⁴ The results of these analyses are shown in Table IV and they accord generally with the work of others.^{24,25}

For compounds 1-4, the methylene proton signals were single sharp lines at room temperature in carbon tetrachloride, while with 4 in dimethyl sulfoxide, hydroxyl exchange was slowed sufficiently so that the methylene signal was split into a doublet corresponding to a J_{HCOH} coupling of 5.3 Hz.

The singlets observed for the methylene protons at room temperature remained unchanged for 1 in vinyl chloride down to -130°, for 2 in the same solvent to -140°, for 3 in dimethyl ether to -130°, and for 4 in carbon disulfide to -40°. Although these results are perhaps not too surprising in view of what has been reported recently,^{4c} at the time the experiments were carried out, we considered some possible explanations of the results which did not require that the barrier to rotation be small, especially for 1. Briefly, these were (1) that the conformation of 1 in the crystal is dictated not by intramolecular but rather by intermolecular forces so that the stable conformation in solution is, in fact, 6; and (2) that the methylene protons might coincidentally have the same shifts even for 8. The arguments against the first proposition are that the crystal structure shows no unusual intermolecular interactions which would favor 8 over 6, although this argument is weakened by not having crystals of 6 and knowing what their structure would be like, and also that 6 would be expected to have very substantial H-2...Br-1 and H-7...Br-2 interactions. The possibility that the chemical shifts would be coincident seems highly unlikely on the basis of a crude ring-current effect calculation which suggests that there should be perhaps 0.15 ppm difference in shift between them. There will also be a substantial influence produced by the bromines on the immediately adjacent hydrogens, of Br-1 on H-8' and of Br-2 on H-1'. Qualitatively, one would expect that these influences on the close protons would be in the same direction (down-field) as the ring-current effect. For this reason, it seems quite unlikely that accidentally coincident chemical shifts are involved, and we conclude that rapid rotation is the correct explanation for the variable-temperature spectra. For 1-3, the free energies of activation for rotation are probably less than 8 kcal/mol.

Registry No.—1, 2025-95-8; 2, 569-41-5; 3, 50585-29-0; 4, 2026-08-6.

References and Notes

- (1) Supported by the National Science Foundation and the Public Health Service through Research Training Grant 5T01 GM-01262-09-13CH to J. S. S.
- (2) Centre D'Etudes Nucléaires de Grenoble, France.
- (3) A very valuable review of the literature on this subject up to 1965 has been prepared by V. Balasubramanian, *Chem. Rev.*, **66**, 567 (1966).
- (4) Especially interesting nmr studies relating to barriers to rotation and conformations of substances of this sort have been reported recently: (a) *aryl-aryl* interactions by H. O. House, W. J. Campbell, and M. Gall, *J. Org. Chem.*, **35**, 1815 (1970), and H. O. House, D. G. Keopsell, and W. J. Campbell, *ibid.*, **37**, 1003 (1972); (b) *alkyl-aryl* interactions by D. L. Fields and T. H. Regan, *J. Org. Chem.*, **36**, 2986, 2991 (1971); see D. L. Fields, T. H. Regan, and R. E. Graves, *ibid.*, **36**, 2995 (1971); (c) *alkyl-alkyl* interactions by J. E. Anderson, R. Franck, and W. Mandella, *J. Amer. Chem. Soc.*, **94**, 4608 (1972), and references cited therein.
- (5) (a) See papers of the systematic investigations of A. I. Kitaigorodskii and Y. T. Struchkov, *Zh. Strukt. Khim.*, **3**, 184 (1962), and references cited therein; (b) G. Gofner and F. H. Herbstein, *Nature (London)*, **200**, 130 (1963), and earlier papers; (c) see also H. D. Rudolph, H. Driegler, A. Jarschbe, and P. Wendling, *Z. Natur-*

- forsch. A*, **22**, 940 (1967); O. Kennard and D. G. Watson, *Mol. Struct. Dimensions*, **1**, 187 (1970).
- (6) J. S. Sherfinski, Ph.D. Thesis, California Institute of Technology, 1973.
- (7) M. B. Jameson and B. R. Penfold, *J. Chem. Soc.*, 528 (1965).
- (8) D. M. Donaldson and J. M. Robertson, *J. Chem. Soc.*, 17 (1953).
- (9) Z. A. Akopyan and Y. T. Struchkov, *Zh. Strukt. Khim.*, **5**, 496 (1964); Z. A. Akopyan, A. I. Kitaigorodskii, and Y. T. Struchkov, *ibid.*, **6**, 729 (1965).
- (10) J. R. Holden and C. Dickinson, *Chem. Commun.*, 144 (1969).
- (11) G. Evard, P. Piret, and M. Van Meerse, *Acta Crystallogr.*, **28**, 497 (1972).
- (12) D. E. Fenton, M. R. Truta, and B. L. Vickery, *Chem. Commun.*, 93 (1971).
- (13) H. Einspahr, J.-B. Robert, R. E. Marsh, and J. D. Roberts, *Acta Crystallogr., Sect. B*, **29**, 1611 (1973).
- (14) W. J. Mitchell, R. D. Topson, and J. Vaughan, *J. Chem. Soc.*, 2526 (1962).
- (15) These cell dimensions agree well with the values reported by Z. A. Akopyan, R. L. Avoyan, and Y. T. Struchkov, *Zh. Strukt. Khim.*, **4**, 772 (1963); $a = 23.56 \text{ \AA}$, $b = 7.67 \text{ \AA}$, $c = 12.54 \text{ \AA}$, $\beta = 95.5^\circ$.
- (16) All calculations were carried out on an IBM 370-155 computer under the CRYM system of crystallographic programs. The quantity minimized in the least-squares calculations was $\sum w(F_o^2 - F_c^2)^2$, with $w = \sigma^{-2}(F_o^2)$.
- (17) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963); A. C. Larson, *ibid.*, **23**, 664 (1967).
- (18) D. W. J. Cruickshank, *Acta Crystallogr.*, **10**, 504 (1957).
- (19) G. S. Pauley and E. A. Yeats, *Acta Crystallogr., Sect. B*, **25**, 2009 (1969).
- (20) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 257-264.
- (21) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
- (22) (a) R. J. Abraham and Z. L. Rossetti, *Tetrahedron Lett.*, 4965 (1972). (b) Similar results have been reported, but not explained in the same way, by R. D. Stolow, T. W. Giants, and J. D. Roberts, *ibid.*, 5777 (1968).
- (23) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1962).
- (24) (a) R. W. Creceley and J. H. Goldstein, *Org. Magn. Resonance*, **2**, 613 (1970); (b) M. W. Jarvis and A. G. Moritz, *Aust. J. Chem.*, **24**, 89 (1971); (c) P. M. E. Lewis, *Tetrahedron Lett.*, 179 (1972).
- (25) (a) L. M. Jackman and S. Sternhell, "International Series of Monographs in Organic Chemistry," 2nd ed., Pergamon Press, Elmsford, N. Y., 1969; (b) J. W. Emsley, S. R. Salman, and R. A. Storey, *J. Chem. Soc. B*, 1513 (1970).

Notes

Kinetics of Hydrolysis of *o*-Tolunitrile in Moderately Concentrated Perchloric Acid Solutions¹

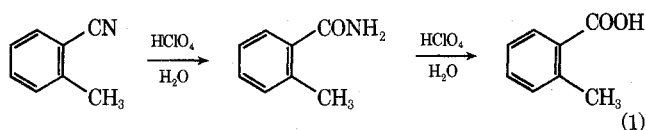
J. F. Bunnett*² and Fredric P. Olsen

*Metcalf Chemical Laboratories, Brown University,
Providence, Rhode Island 02912*

Received July 26, 1973

A kinetic study of the hydrolysis of benzonitrile was recently published by Hyland and O'Connor.³ This prompts us to report a set of data obtained some years ago⁴ concerning rates of hydrolysis of *o*-tolunitrile in HClO₄ solutions at 133.5°.

The hydrolysis reaction is represented in eq 1. An analytical technique was chosen that reveals only destruction of the nitrile and is insensitive to further hydrolysis of amide to acid. The data obtained in 1.5-6 M HClO₄ solutions are listed in Table I.



These data are correlated quite well by the linear free energy relationship (LFER) of eq 2, in which H_0 is the Hammett acidity function, k_ψ is the measured pseudo-first-order rate constant at any acid concentration, and k_2^0 is the second-order rate constant (first order in substrate, first order in H⁺) at infinite dilution in water as reference state.⁵ The correlation and the resulting parameters are summarized in Table II. The slope (ϕ value) is +0.61.

$$\log k_\psi + H_0 = \phi(H_0 + \log[H^+]) + \log k_2^0 \quad (2)$$

Correlation of $\log k_\psi + H_0$ with $\log a_w$,⁶ where a_w is the activity of water, was also attempted. That correlation is also summarized in Table II. The slope (w value) is +3.33. As revealed particularly by the standard deviations of points from the linear regression lines, σ_y , the correlation with $\log a_w$ is less satisfactory than with $(H_0 + \log[H^+])$. A plot of the correlation with $\log a_w$ shows slight but persistent curvature, whereas the LFER plot is

Table I
Kinetics of Hydrolysis of *o*-Tolunitrile in Aqueous Perchloric Acid at 133.5°

[HClO ₄], M	10 ⁶ k_ψ , sec ⁻¹ ^a	H_0	$H_0 + \log[H^+]$
1.47	2.12 ± 0.06	-0.59	-0.41
3.01	6.42 ± 0.43	-1.33	-0.86
4.00	12.5 ± 0.55	-1.79	-1.18
4.51	16.0 ± 0.35	-2.02	-1.38
4.99	19.8 ± 0.53	-2.28	-1.58
5.50	32.0 ^b	-2.59	-1.85
6.02	38.3 ± 1.15	-2.90	-2.12

^a Standard deviations are shown. ^b Average of 31.7 ± 0.7 and 32.3 ± 1.4.

Table II
Summary of Rate Correlations

Correlation	Slope	Intercept	σ_y^a	σ_{sl}^b	r^c
($\log k_\psi + H_0$) vs. ($H_0 + \log[H^+]$)	+0.61 ^d	-4.99	0.03	0.02	0.997
($\log k_\psi + H_0$) vs. $\log a_w$	+3.33 ^e	<i>f</i>	0.04	0.16	0.994
$\log k_\psi$ vs. $-H_0$	+0.55	<i>f</i>	0.05	0.03	0.994

^a Standard deviation of points, in the y direction, from the linear regression line. ^b Standard deviation of slope. ^c Correlation coefficient. ^d ϕ value. ^e w value. ^f Not listed; has no fundamental significance.

straight except for small random deviations most likely due to experimental error.

Correlation of $\log k_\psi$ with $-H_0$ ⁷ was also attempted, and the correlation is summarized in Table II. The σ_y values show that this correlation gives the least satisfactory fit of experimental points to a straight line. The slope is 0.55.

The H_0 values⁸ and $\log a_w$ values⁶ employed in these correlations are for 25° or thereabouts, while the reactions were conducted at 133.5°. Also, acid concentrations were not corrected for thermal expansion of the reaction solutions from room to reaction temperature. The magnitudes of the slopes and intercepts may therefore be somewhat affected. The ϕ parameters measured by Hyland and