

seen in the more asymmetric molecule where one of the O...O distances is shorter than any of those observed in the molecules with a single *ortho* hydroxyl group. The reason for this apparent strengthening is not obvious.

Financial support of the National Science Foundation (NSF 77-08325) is greatly acknowledged.

#### References

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.

IRIE, T. & KAMETANI, M. (1979). *Chem. Abstr.* No. 169291q (Japanese patent).

KATO, V. K. (1971). *Acta Cryst.* **B27**, 2028–2034.

LIEBICH, B. W. (1976). *Acta Cryst.* **B32**, 431–435.

LIEBICH, B. W. (1979). *Acta Cryst.* **B35**, 1186–1190.

LIEBICH, B. W. & PARTHÉ, E. (1974). *Acta Cryst.* **B30**, 2522–2524.

SEMMINGSEN, D. (1972). *Acta Chem. Scand.* **26**, 143–154.

WILLIAMS, D. E. (1966). *Acta Cryst.* **21**, 340–349.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

*Acta Cryst.* (1982). **B38**, 559–564

## The Structures of 1,8-Dimorpholinonaphthalene and 1,8-Dipiperidinonaphthalene

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(Received 1 April 1981; accepted 31 July 1981)

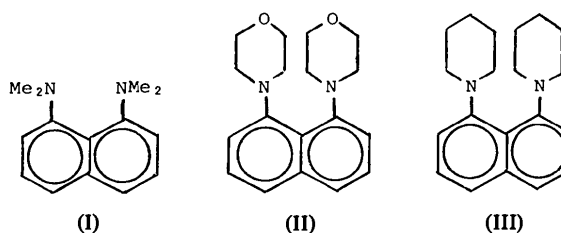
#### Abstract

The structures of 1,8-dimorpholinonaphthalene (II) and 1,8-dipiperidinonaphthalene (III) have been determined. (II),  $C_{18}H_{22}N_2O_2$ ,  $M_r = 298.4$ , is monoclinic,  $P2_1/c$ , with  $a = 11.086$  (2),  $b = 9.870$  (1),  $c = 16.378$  (3) Å,  $\beta = 121.2$  (3)°,  $V = 1532.9$  Å<sup>3</sup>,  $Z = 4$ ,  $d_c = 1.29$  g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 6.68$  cm<sup>-1</sup>. 1508 reflections were of significant intensity. The final  $R$  value is 0.059. (III),  $C_{20}H_{26}N_2$ ,  $M_r = 294.2$ , is triclinic,  $P\bar{1}$ , with  $a = 9.151$  (2),  $b = 9.380$  (2),  $c = 10.118$  (3) Å,  $\alpha = 105.9$  (5),  $\beta = 98.8$  (4),  $\gamma = 94.2$  (4)°,  $V = 819.2$  Å<sup>3</sup>,  $Z = 2$ ,  $d_c = 1.19$  g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 5.38$  cm<sup>-1</sup>. 1956 reflections were of significant intensity. The final  $R$  value is 0.066. Both are strong bases in aqueous solution as is the bis(dimethylamino) analog (I). As expected, the naphthalene system is distorted in both (II) and (III) due to overcrowding. A survey of analyses of structures containing morpholine or piperidine rings shows both to be flexible. (II) shows the most pyramidal (least coplanar) bonds around nitrogen of any morpholine derivative previously studied. On the other hand, (III) is less pyramidal at nitrogen than are some other known structures containing the piperidine moiety. Possibly intermolecular forces acting on substituents in the 4-carbon position are responsible.

#### Introduction

In our continuing study of the unusual acid–base properties of substances related to 1,8-bis(dimethyl-

amino)naphthalene (I) (Alder, Bowman, Steele & Winterman, 1968; Hibbert, 1973, 1974; Einspahr, Robert, Marsh & Roberts, 1973) we have examined the proton-transfer reactions (Awwal, Burt & Kresge, 1981) and determined the crystal structures of 1,8-dimorpholinonaphthalene (II) and 1,8-dipiperidinonaphthalene (III). These studies form part of an attempt to relate the molecular structures of these materials to their acid–base behavior.



#### 1,8-Dimorpholinonaphthalene (II)

##### Experimental

Needle-shaped crystals prepared by treating 1,8-diaminonaphthalene with 2,2'-dichlorodiethyl ether (Awwal, Burt & Kresge, 1981) were initially subjected to X-ray photographic examination. Cell parameters were determined from  $\chi$ ,  $\varphi$  and  $2\theta$  settings of 12 reflections on a Picker four-circle diffractometer using Ni-filtered Cu  $K\alpha$  radiation.

A crystal of dimensions  $ca\ 0.08 \times 0.40 \times 0.05$  mm was used for data collection on the diffractometer in the  $2\theta$ - $\theta$  scan mode. 2785 reflections were recorded to a maximum  $\theta$  angle of  $61^\circ$  at a scan speed of  $2^\circ\ \text{min}^{-1}$ . The scan range was  $2^\circ$  at low  $2\theta$ . Each background count was for 60 s. Of the recorded reflections 1508 were deemed significant on the criterion  $I > 2\sigma(I)$  where  $\sigma(I) = [a(\text{peak} + \text{bckgd}) + aI^2 + 0.02I]$  where  $a$  is the attenuation factor;  $\sigma(F_o)$  was taken as  $\{[\sigma(I)/Lp] + 0.02F_o^4\}^{1/2}/2F_o$ ,  $Lp$  being the Lorentz-polarization factor; the term  $0.02F_o^4$  makes allowance for instrumental instability. The crystal appeared to be quite stable to X-irradiation. No absorption corrections were made.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) (with  $B_{eq}$  values for nonhydrogen atoms) for compound (II)

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	$x$	$y$	$z$	$B_{eq}$ ( $\text{\AA}^2$ )
C(1)	5376 (3)	4128 (4)	7137 (2)	2.7 (1)
C(2)	6314 (4)	4534 (4)	6876 (3)	3.7 (1)
C(3)	7792 (4)	4611 (4)	7542 (3)	4.1 (1)
C(4)	8290 (4)	4202 (4)	8453 (3)	3.8 (1)
C(5)	7959 (4)	3429 (4)	9731 (3)	3.8 (1)
C(6)	7126 (4)	3144 (5)	10083 (3)	4.1 (1)
C(7)	5648 (4)	3284 (4)	9499 (2)	3.5 (1)
C(8)	5015 (3)	3671 (4)	8551 (2)	2.7 (1)
C(9)	5868 (3)	3862 (4)	8129 (2)	2.6 (1)
C(10)	7376 (3)	3827 (4)	8768 (3)	3.0 (1)
C(11)	3478 (4)	4552 (4)	5484 (3)	3.8 (1)
C(12)	1890 (4)	4433 (4)	4850 (3)	4.3 (1)
C(13)	1901 (4)	2427 (4)	5607 (3)	3.8 (1)
C(14)	3475 (3)	2518 (4)	6282 (2)	3.1 (1)
C(15)	2743 (4)	3381 (4)	8433 (3)	3.6 (1)
C(16)	1167 (4)	3596 (5)	7741 (3)	4.3 (1)
C(17)	1598 (4)	5543 (4)	7129 (3)	3.9 (1)
C(18)	3182 (3)	5363 (4)	7775 (3)	3.1 (1)
N(1)	3920 (3)	3949 (3)	6418 (2)	2.7 (0)
N(2)	3525 (3)	3921 (3)	8008 (2)	2.6 (0)
O(1)	1457 (3)	3048 (3)	4703 (2)	4.5 (0)
O(2)	844 (3)	4999 (3)	7540 (2)	4.4 (1)
H(2)	5953	4758	6177	
H(3)	8445	4993	7340	
H(4)	9354	4129	8912	
H(5)	9013	3394	10163	
H(6)	7541	2766	10746	
H(7)	5057	3087	9775	
H(11A)	3930	4048	5180	
H(11B)	3778	5522	5571	
H(12A)	1595	4895	4224	
H(12B)	1452	4950	5167	
H(13A)	1617	1448	5489	
H(13B)	1418	2875	5910	
H(14A)	3963	1993	6014	
H(14B)	3724	2112	6915	
H(15A)	2937	2396	8576	
H(15B)	3017	3881	9041	
H(16A)	872	3098	7123	
H(16B)	612	3202	8016	
H(17A)	1290	5094	6495	
H(17B)	1376	6550	6996	
H(18A)	3689	5731	7461	
H(18B)	3511	5896	8385	

The structure was determined by *MULTAN* (Germain, Main & Woolfson, 1971) using 275 reflections with  $|E| > 1.4$ . The phase set with the highest figure of merit (1.1) was used for the  $E$  map. This revealed 18 of the 22 nonhydrogen atoms in stereochemically reasonable positions. Refinement by Fourier and least-squares techniques [using *XRFLS* (Busing, Martin & Levy, 1963) and scattering factors of Cromer & Mann (1968)] was uneventful. All H atoms were found on the difference map. They were fixed in theoretical positions with C-H distances set to  $1.0\ \text{\AA}$  and isotropic  $B$  factors set to  $6\ \text{\AA}^2$ . The final  $R$  was 0.059. Final atomic coordinates and equivalent temperature factors are given in Table 1.\*

### 1,8-Dipiperidinonaphthalene (III)

#### Experimental

The crystals, which are colorless and needle-shaped, were prepared from 1,8-diaminonaphthalene and 1,5-dibromopentane in a manner similar to that given for compound (II). Preliminary examination was performed as described for compound (II).

A crystal  $ca\ 0.16 \times 0.48 \times 0.09$  mm was used for data collection. Other details of data collection were similar to those described for compound (II). Compound (III) was also stable to X-irradiation. Of 2561 independent reflections 1956 had  $I > 2\sigma(I)$  and were used for structure analysis.

The structure determination was not straightforward. Intensity statistics implied hypercentricity. However the best  $E$  map obtained using *MULTAN* gave peaks which could be interpreted as two overlapping molecular images  $A$  and  $B$  (Fig. 2). That this did not represent a genuinely disordered structure was confirmed by the model failing to refine below  $R = 0.25$ . Two other possibilities were: (a) the structure is  $P1$  with one genuine molecular pair  $AB'$  (or  $A'B$ ) and the other pair spurious or (b) the molecular pairing as (a) but belonging strictly to  $P\bar{1}$  (with a non-origin crystallographic center between the pair). Both structural models were subjected to anisotropic least-squares refinement of the non-hydrogen atoms together with idealized positions and isotropic temperature factors for the H atoms. The  $R$  values were 0.059 ( $P1$ ) and 0.066 ( $P\bar{1}$ ) respectively. Model (a) had unacceptable bond lengths and angles and lacked a pseudo diad axis

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond angles for (II) and (III) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36375 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of molecular symmetry. The latter model, on the other hand, had a rational geometry and a good diad axis based on *BMFIT* (Yuen & Nyburg, 1979). The maximum deviation from this symmetry was 0.039 Å and the sum of the squared displacements,  $\Delta^2 = 0.006 \text{ \AA}^2$ . The crystallographic center of symmetry refined to (-0.0256, -0.0131, -0.0763).<sup>\*</sup> Following

<sup>\*</sup> Note added in proof: This is equivalent to taking the geometric mean of models *A* and *B*. This procedure has been adopted by others. See, for example, Duffin (1968) and Bürgi & Dunitz (1971).

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) (with  $B_{eq}$  values for nonhydrogen atoms) for compound (III)

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$ (Å <sup>2</sup> )
C(1)	2633 (3)	3913 (3)	4728 (3)	3.1 (0)
C(2)	2965 (3)	5014 (4)	4113 (3)	4.2 (0)
C(3)	2950 (4)	4703 (4)	2679 (4)	4.9 (1)
C(4)	2529 (4)	3299 (4)	1830 (3)	4.7 (1)
C(5)	1734 (4)	652 (4)	1465 (3)	4.6 (0)
C(6)	1478 (4)	-526 (4)	1967 (3)	4.6 (0)
C(7)	1794 (3)	-325 (3)	3404 (3)	4.0 (0)
C(8)	2274 (3)	1049 (3)	4366 (3)	3.1 (0)
C(9)	2378 (3)	2359 (3)	3874 (3)	3.1 (0)
C(10)	2216 (3)	2105 (4)	2397 (3)	3.8 (0)
C(11)	3039 (4)	5848 (3)	6965 (3)	4.2 (0)
C(12)	3072 (4)	5087 (3)	8510 (3)	5.0 (1)
C(13)	1523 (4)	5664 (4)	8795 (3)	5.2 (1)
C(14)	913 (4)	4087 (3)	7892 (3)	4.2 (0)
C(15)	974 (3)	3894 (3)	6360 (3)	3.5 (0)
C(16)	2240 (4)	-177 (3)	6209 (3)	3.8 (0)
C(17)	2521 (4)	137 (3)	7779 (3)	4.2 (0)
C(18)	4153 (4)	676 (4)	8391 (3)	4.7 (1)
C(19)	4650 (3)	2029 (3)	7941 (3)	4.0 (0)
C(20)	4288 (3)	1715 (3)	6360 (3)	3.4 (0)
N(1)	2502 (2)	4297 (2)	6164 (2)	3.0 (0)
N(2)	2695 (2)	1160 (2)	5807 (2)	2.9 (0)
H(2)	3132	6037	4591	
H(3)	3271	5442	2233	
H(4)	2474	3068	743	
H(5)	1530	481	458	
H(6)	1232	-1640	1358	
H(7)	1461	-1133	3698	
H(11A)	4093	6183	6975	
H(11B)	2407	6648	6758	
H(12A)	3351	7077	9221	
H(12B)	3601	5319	8922	
H(13A)	1279	5734	9767	
H(13B)	681	6335	8436	
H(14A)	1573	3426	8233	
H(14B)	-154	3765	7938	
H(15A)	335	4619	6069	
H(15B)	634	2880	5840	
H(16A)	2886	-975	5878	
H(16B)	1191	-526	5820	
H(17A)	1874	1003	8223	
H(17B)	2153	-723	8106	
H(18A)	4469	936	9403	
H(18B)	4798	-121	7931	
H(19A)	4253	2959	8440	
H(19B)	5853	2345	8247	
H(20A)	4506	2639	6067	
H(20B)	4888	932	5902	

refinement, the independent molecule was translated by the above vector (with sign reversed) to bring the center of symmetry to the origin. The failure of *MULTAN* to generate the correct phases is presumably connected with the coincidence of several atoms in the *A* and *B* images of the molecule (Fig. 2).

Final atomic coordinates and equivalent values of the anisotropic temperature factors are given in Table 2.<sup>\*</sup>

## Discussion

Fig. 1 shows the bond lengths for the non-hydrogen atoms of compound (II); Fig. 3 gives the bond lengths for compound (III). (Bond angles have been deposited.) Both sets of bond lengths appear normal.

The primary purpose of this study was to discover whether there are any unusual structural effects which could account for the remarkable basicity of compounds (II) and (III). [In addition, confirmation of the molecular structure of (II) was needed.] Numerous crystal structure analyses indicate the presence of steric interactions between bulky *peri* substituents of naphthalene nuclei. These interactions can lead to three types of distortion of the naphthalene nucleus. Writing the substituents at C(1)/(8) as *Z*(1)/(8) (where the slash means 'or') these three distortions are: (i) lack of collinearity of *Z*(1)/(2)-C(1)/(8)-C(4)/(5); (ii) a non-zero torsion angle *Z*(1)-C(1)-C(8)-*Z*(2); (iii) non-zero torsion angles C(1)/(8)-C(9)-C(10)-C(4)/(5). These distortions are given for the four molecules (I), (II), (III) and 1,3,6,8-tetra-*tert*-butylnaphthalene

<sup>\*</sup> See deposition footnote.

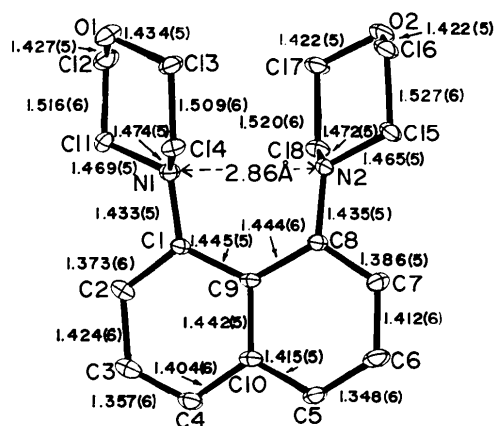


Fig. 1. ORTEP plot (Johnson, 1965) of compound (II) showing atomic numbering, bond lengths (Å) and 50% probability ellipsoids.

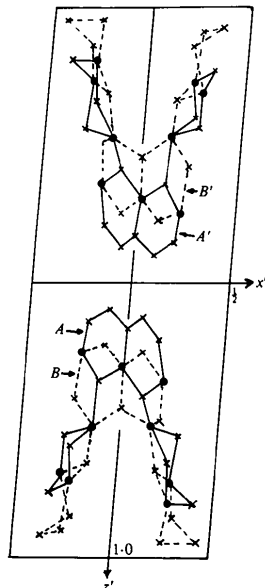


Fig. 2. False structure of compound (III) obtained from *MULTAN* phases. Coincident atomic images are marked by filled circles.

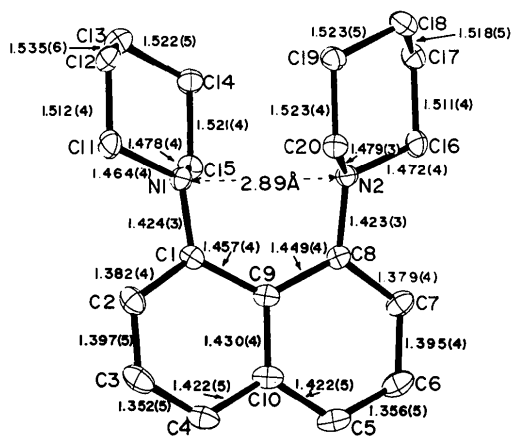


Fig. 3. *ORTEP* plot (Johnson, 1965) of compound (III) showing atomic numbering, bond lengths (Å) and 50% probability ellipsoids.

(Blount, Cozzi, Damewood, Iroff, Sjöstrand & Mislow, 1980) in Table 3. The ordering of the compounds in the table is such as to indicate increasing intramolecular interaction. The *tert*-butyl derivative is probably the most distorted molecule of this class examined so far.

Both molecules (II) and (III) have noncrystallographic pseudo diad axes of symmetry about C(9)–C(10) (*BMFIT*, Yuen & Nyburg, 1979). Details for (III) are given above. For (II) the maximum deviation from twofold symmetry is 0.034 Å and  $\Delta^2 = 0.0045 \text{ \AA}^2$ . The molecules have very similar geometries with maximum deviations of the nonhydrogen atoms of 0.14 Å and  $\Delta^2 = 0.123 \text{ \AA}^2$ .

Table 3. Distortions of the naphthalene framework in certain 1,8-disubstituted naphthalenes

The substituent at the 1 or 8 position is Z. Column (i), angles Z(1)/(2)–C(1)/(8)–C(4)/(5); column (ii), the torsional angle Z(1)–C(2)–C(8)–Z(2); column (iii), the torsional angles C(1)/(8)–C(9)–C(10)–C(4)/(5).

	(i) (°)	(ii) (°)	(iii) (°)	References
Compound (II)	173.1 173.8	–18.97 8.79	7.76 8.79	(a)
Compound (I)	173.3 173.9	–20.37 10.49	8.91 10.49	(b)
Compound (III)	172.4 173.3	–21.61 10.2	9.77 10.2	(c)
1,3,6,8-Tetra- <i>tert</i> -butylnaphthalene	151.0	–64.7	15.0	(d)

References: (a) this work, (b) calculated from Einspahr *et al.* (1973), (c) this work, (d) Blount *et al.* (1980).

Table 4. Short H...H distances in compounds (II) and (III)

	(II)	(III)	
Hetero ring to naphthalene ring			
H(7)...H(15B)	2.087	H(7)...H(16B)	2.123
H(2)...H(11A)	2.095	H(2)...H(11B)	2.322
H(2)...H(11B)	2.210	H(7)...H(16A)	2.346
H(7)...H(15A)	2.249	H(2)...H(11A)	2.401
Hetero ring to hetero ring			
H(12B)...H(17A)	2.278	H(12B)...H(18A)	2.276
H(13B)...H(16A)	2.368	H(14A)...H(17A)	2.306

We have listed the distortions of the naphthalene ring in four compounds disubstituted with bulky *peri* substituents (Table 3). The dipiperidine derivative (III) has a more distorted naphthalene ring than (II). This is correlated with the N...N and H...H intramolecular distances. In (II) N...N has the shorter distance [2.856 (5) *vs.* 2.887 (3) Å, Fig. 3], and, as Table 4 shows, the H...H distances on the whole are also shorter in (II) than in (III). Clearly, the shorter these distances, the less distorted is the naphthalene ring.

Two other criteria for ring–substituent interaction are: (i) the bond angles subtended at the N atoms and (ii) the deviations of the atoms in 1 and 4 positions from the mean plane of the remaining four C atoms in the ring. A survey of known structure analyses involving morpholine or piperidine derivatives shows how variable is the pyramidal nature of the bonds attached to the N atom. Table 5 lists the sum of the angles at N (in approximately descending order) for several morpholine derivatives and Table 6 lists the corresponding data for piperidine derivatives. Apart from the study of Kijima, Sakaguchi & Iitaka (1973), all published analyses indicate that the morpholine ring has the chair conformation. In two structures having the sum of bond angles at N close to 360° we calculate

deviations of N and O from the mean four-carbon-atom plane to be 0.681, -0.757 Å and 0.600, -0.686 Å (Husebye, 1973) and 0.662, -0.661 Å (Kerr & Van Roey, 1979) which compare well with our data for compound (II): 0.663, -0.651 Å and -0.680, 0.655 Å. Thus, despite the virtual coplanarity of the bonds to N in the structures of Husebye (1973) and of Kerr & Van Roey (1979), the chair conformation is virtually identical to that found in our structure (II) where the bonds at N are far from coplanar. In the morpholine ring studied by Kijima, Sakaguchi & Iitaka (1973) the N and O deviations from the four-carbon mean plane are only -0.087 and 0.133 Å respectively. Such a morpholine ring would be nearly coplanar. These authors comment on the large anisotropic temperature factors of the four C atoms. However, on the basis of results for related structures we believe that these anisotropic factors are not genuine and that the structure is disordered, the ring actually having a chair conformation but occupying two possible positions.

The range of variation in the sum of the bond angles at N is again striking for piperidine derivatives (Table 6). (In this survey we have excluded pyridinium compounds and those in which intra- or intermolecular hydrogen bonds are present.) Compound (III), however, is no longer that showing the smallest sum. A possible reason is that each of the three compounds

listed as having the sum of bond angles at N less than those in (III) has a bulky substituent (or substituents) attached at the 4-carbon position of the piperidine ring. These bulky substituents could be subject to packing forces which are transmitted to the piperidine ring. Morpholine, in which oxygen occupies the 4 position, cannot have such derivatives and it is thus not surprising that of all the morpholine derivatives studied, our compound (II) is the most distorted.

The structure of the cation of (I) is known from two analyses (Truter & Vickery, 1972). In these, the N...N distances are 2.65 (2) and 2.60 (1) Å, significantly shorter than that, 2.79 (5), found in the unprotonated molecule (I) (Einspahr, Robert, Marsh & Roberts, 1973). The comparable distances of 2.856 (5) and 2.887 (3) Å in molecules (II) and (III) imply that the same efficient hydrogen bonding can take place in aqueous solution and cause the strong basicity. No other special stereochemical features seem to be involved.

Financial assistance from the Natural Sciences and Engineering Research Council of Canada, from the Petroleum Research Fund of the American Chemical Society and the Connaught Fund of the University of Toronto (to AA, RJ and AJK) is gratefully acknowledged.

Table 5. *Sum of bond angles at N for morpholine derivatives (°)*

4-(2-Hydroxythiobenzoyl)morpholine	360	Kerr & Van Roey (1979)
4-Bromo-2-[(4-methyl-2-morpholino-1H-5-imidazolyl)methylene]-1-oxo-1,2-dihydro-naphthalene	359	Kijima, Sakaguchi & Iitaka (1973)
Bis[morpholino(thio)oxo]methyl trisulfide	357.6 } 359.8 }	Husebye (1973)
Morpholine biguanide hydrobromide	359.3 } 359.1 }	Handa & Saha (1973)
Tetrakis(4-morpholinecarbodithioato)tellurium(IV)	358.9 } 357.9 } 359.8 }	Esperàs & Husebye (1973)
$\beta$ -Chloromethylsulfonyl- $\beta$ -methyl- $\alpha$ -morpholinostyrene	357.5	Del Buttero, Maiorana, Andreotti, Bocelli & Sgarabotto (1975)
1,1,2-Trimorpholinoethene	348.3	Albinati & Zocchi (1974)
Di-4-morpholinyl disulfide	342.2 } 344.1 }	Nyburg & Pickard (1973)
2-(2-Morpholinocyclohexen-3-ylsulfonyl)ethanenitrile	341.3	Sammes, Harlow & Simonsen (1976)
Di-4-morpholinyl tetrasulfide	345.1	Foss & Janickis (1980)
1,8-Dimorpholinonaphthalene	337.1 } 337.6 }	This paper, compound (II)

Table 6. *Sum of bond angles at N for piperidine derivatives (°)*

1,1'-Thiobis(thiocarbonyl)dipiperidine	360	Johnson & Paul (1970)
Piperidinothiosemicarbazide	360	Koo & Chang (1975)
1-[ <i>p</i> -(Piperidinocarbonyl)methoxy]phenyl]acetaldehyde oxime	359.2	Tranqui, Cromer & Boucherle (1974)
1,8-Dipiperidinonaphthalene	340.1 } 337.9 }	This paper, compound (III)
3-(1-Benzyl-4-piperidyl)-3-phenyl-2,6-piperidinedione	333.9	Koch (1973)
1-[ <i>p</i> -(Piperidinocarbonyl)methoxy]phenyl]formaldehyde oxime	330.6	Michel, Evrard, Schlitz, Durant & Koch (1976)
<i>N</i> -[4-(Methoxymethyl)-1-(2-phenylethyl)-4-piperidyl]- <i>N</i> -phenylpropanamide	327.0	Koch, De Ranter, Rolies & Dideberg (1976)

## References

- ALBINATI, S. A. & ZOCCHI, M. (1974). *Acta Cryst.* **B30**, 544–546.
- ALDER, R. W., BOWMAN, P. S., STEELE, W. R. S. & WINTERMAN, D. R. (1968). *Chem. Commun.* pp. 723–724.
- AWWAL, A., BURT, R. A. & KRESGE, A. J. (1981). *J. Chem. Soc. Perkin Trans. 2*. In the press.
- BLOUNT, J. F., COZZI, J. R., DAMEWOOD, J. R. JR, IROFF, L. D., SJÖSTRAND, U. & MISLOW, K. (1980). *J. Am. Chem. Soc.* **102**, 99–103.
- BÜRGI, H. B. & DUNITZ, J. D. (1971). *Acta Cryst.* **A27**, 117–119.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1963). *XRFLS*, an extensively modified version of *ORFLS*; Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DEL BUTTERO, P., MAIORANA, S., ANDRETTI, G. O., BOCELLI, G. & SGARABOTTO, P. (1975). *J. Chem. Soc. Perkin Trans. 2*, pp. 809–816.
- DUFFIN, B. (1968). *Acta Cryst.* **B24**, 1256–1261.
- EINSPAHR, H., ROBERT, J.-B., MARSH, R. E. & ROBERTS, J. D. (1973). *Acta Cryst.* **B29**, 1611–1617.
- ESPERÅS, S. & HUSEBYE, S. (1973). *Acta Chem. Scand.* **27**, 706–707.
- FOSS, O. & JANICKIS, V. (1980). *J. Chem. Soc. Dalton Trans.* pp. 632–633.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HANDA, R. & SAHA, N. N. (1973). *Acta Cryst.* **B29**, 554–560.
- HIBBERT, F. (1973). *Chem. Commun.* p. 463.
- HIBBERT, F. (1974). *J. Chem. Soc. Perkin Trans. 2*, pp. 1862–1866.
- HUSEBYE, S. (1973). *Acta Chem. Scand.* **27**, 756–762.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- JOHNSON, P. L. & PAUL, I. C. (1970). *J. Chem. Soc. B*, pp. 1296–1303.
- KERR, K. A. & VAN ROEY, P. M. A. O. (1979). *Acta Cryst.* **B35**, 2727–2729.
- KIJIMA, K., SAKAGUCHI, T. & IITAKA, Y. (1973). *Chem. Pharm. Bull.* **21**, 2529–2537.
- KOCH, M. H. J. (1973). *Acta Cryst.* **B29**, 369–371.
- KOCH, M. H. J., DE RANter, C. J., ROLIES, M. & DIDEBERG, O. (1976). *Acta Cryst.* **B32**, 2529–2531.
- KOO, C. H. & CHANG, C. H. (1975). *J. Korean Chem. Soc.* **19**, 85–91.
- MICHEL, A. G., EVRARD, G., SCHILTZ, M., DURANT, F. & KOCH, M. H. J. (1976). *Acta Cryst.* **B32**, 2507–2509.
- NYBURG, S. C. & PICKARD, F. H. (1973). *J. Cryst. Mol. Struct.* **3**, 343–348.
- SAMMES, M. P., HARLOW, R. L. & SIMONSEN, S. H. (1976). *J. Chem. Soc. Perkin Trans. 2*, pp. 1126–1130.
- TRANQUI, D., CROMER, D. T. & BOUCHERLE, A. (1974). *Acta Cryst.* **B30**, 2237–2240.
- TRUTER, M. R. & VICKERY, B. L. (1972). *J. Chem. Soc. Dalton Trans.* pp. 395–403.
- YUEN, P.-S. & NYBURG, S. C. (1979). *J. Appl. Cryst.* **12**, 258.

*Acta Cryst.* (1982). **B38**, 564–570

## The Structure of a Dinucleoside Monophosphate Having a High-*anti* Conformation: 8,2'-*S*-Cyclo-2'-thioadenylyl(3'-5')-8,2'-*S*-cyclo-2'-thioadenosine (A<sup>s</sup>pA<sup>s</sup>) Hydrochloride

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(Received 18 June 1981; accepted 5 August 1981)

### Abstract

The crystal and molecular structure of 8,2'-*S*-cyclo-2'-thioadenylyl(3'-5')-8,2'-*S*-cyclo-2'-thioadenosine (A<sup>s</sup>pA<sup>s</sup>) hydrochloride,  $2(\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_8\text{PS}_2^+\cdot\text{Cl}^-)\cdot 5\text{H}_2\text{O}$ , has been determined by X-ray diffraction methods and refined to an *R* value of 0.078. A<sup>s</sup>pA<sup>s</sup> crystallizes in the triclinic space group *P*1, with unit-cell

0567-7408/82/020564-07\$01.00

dimensions:  $a = 11.161(4)$ ,  $b = 11.824(4)$ ,  $c = 12.136(3)$  Å,  $\alpha = 89.20(3)$ ,  $\beta = 97.92(3)$  and  $\gamma = 116.75(2)^\circ$ ;  $Z = 1$ ,  $D_m = 1.655(4)$ ,  $D_x = 1.656$  g cm<sup>-3</sup>,  $\sin \theta/\lambda = 0.595$  Å<sup>-1</sup>. The molecular conformations of two independent A<sup>s</sup>pA<sup>s</sup> molecules in an asymmetric unit are almost identical, and are both in the sharp 'bend' conformation. *i.e.* the rotation ( $\omega'$ ,  $\omega$ ) around the P–O bond is ( $g^-$ ,  $t$ ) rather than the preferred ( $g^-$ ,  $g^-$ ) or

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