

Fig. 2. Molecular packing.

zwitterionic thiazolium resonance structure. In contrast to these bond distances, in (2) the C3—O1 bond length of 1.205 (2) Å has double-bond character and the two endocyclic N—C distances [N1—C2 = 1.391 (2), N1—C3 = 1.389 (2) Å] agree with each other and are typical for N—C single bonds (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). All geometric bonding parameters of the 2-oxo-thiazoline moiety in the latter above-mentioned com-

pound agree well with those in (2), except the C1—C2 bond length of 1.401 (10) Å. This bond belongs to both the aromatic benzene and the thiazolone rings and is elongated by 0.049 Å compared with the C1—C2 distance of 1.352 (2) Å in (2), which corresponds to an isolated double bond.

All other geometrical parameters in (2) are in agreement with expectation. Intermolecular contacts are consistent with van der Waals radii. The molecular packing is shown in Fig. 2.

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#### References

- ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- AUGUSTIN, M. & DÖLLING, W. (1990). *Z. Chem.* **30**, 395–403.
- AUGUSTIN, M., DÖLLING, W. & RUDORF, W.-D. (1989). *Z. Chem.* **29**, 445–446.
- JASKÓLSKI, M. (1982). *EDIT*. Program to edit atomic information from atom data files. Univ. of Poznań, Poland.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination, Univ. of Cambridge, England.
- SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
- SHIN, W. & KIM, Y. C. (1986). *J. Am. Chem. Soc.* **108**, 7078–7082.
- STANKOVIĆ, S. & ANDRETTI, G. D. (1979). *Acta Cryst.* **B35**, 3078–3080.
- VRÁBEL, V., LOKAJ, J., KELLÖ, E., KONEČNÝ, V., BATSANOV, A. C. & STRUCHKOV, YU. T. (1990). *Acta Cryst.* **C46**, 470–472.

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## Structures of 3-Methoxypyrazine 1-Oxide (1a) and 3-Methoxy-5-methylpyrazine 1-Oxide (1b)

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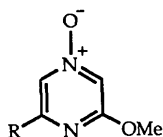
**Abstract.** (1a), C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>, *M<sub>r</sub>* = 126.1, triclinic, *P* $\bar{1}$ , *a* = 12.094 (1), *b* = 14.689 (1), *c* = 7.0228 (4) Å,  $\alpha$  = 96.991 (6),  $\beta$  = 101.856 (4),  $\gamma$  = 101.361 (7)°, *V* = 1179.8 (4) Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.420 g cm<sup>-3</sup>,  $\lambda$ (Cu *K*α) = 1.54178 Å,  $\mu$  = 9.11 cm<sup>-1</sup>, *F*(000) = 528, *T* =

293 K, *R* = 0.061 for 1544 observed [*I*/ $\sigma$ (*I*) ≥ 3] reflexions. (1b), C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>, *M<sub>r</sub>* = 140.1, orthorhombic, *Pna*2<sub>1</sub>, *a* = 8.0056 (5), *b* = 12.7140 (6), *c* = 6.6861 (9) Å, *V* = 680.5 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.368 g cm<sup>-3</sup>,  $\lambda$ (Mo *K*α) = 0.71069 Å,  $\mu$  = 0.98 cm<sup>-1</sup>, *F*(000) = 296, *T* = 294 K, *R* = 0.032 for 877 observed [*I*/ $\sigma$ (*I*) ≥ 3] reflexions. Each *N*-oxide,

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(1a) and (1b), is essentially planar, the methoxyl methyl groups lying in the plane of the heterocyclic rings. The structures of these oxides demonstrate that steric rather than electronic factors govern the regiochemistry of *N*-oxidation of unsymmetrical pyrazines.

**Introduction.** An  $\alpha$ -methyl group (inductively) and a  $\gamma$ -methoxyl group (mesomerically) stabilize positive charge on the N atom in pyridine, thus the  $pK_a$ 's (Katritzky, 1963) of 2-methylpyridine (5.97) and of 4-methoxypyridine (6.62) show both to be stronger bases than pyridine itself (5.23); 2-methoxypyridine, in which the mesomeric effect can also stabilize adjacent protonation, is nonetheless a weaker base (3.28) presumably due to the larger influence of a combination of inductive and steric effects. It is difficult, then, to be sure from the corresponding basicity values for 2-methylpyrazine (1.45) and 2-methoxypyrazine (0.75), *versus* 0.65 for pyrazine itself, whether these derivatives protonate at N1 or N4. In any case the pattern of electrophilic addition to azine N atoms does not necessarily follow protonation trends in a straightforward manner, for example, ratios for quaternization of 2-methylpyrazine with iodomethane at N1 and N4 vary from 1:4 (Deady & Zoltewicz, 1971) to 1:1 (Jovanovich, 1985) according to the exact reaction conditions; reaction of 2-methoxypyrazine with iodomethane produced only the 4-metho salt (Deady & Zoltewicz, 1971). Since pyrazines are intrinsically less reactive (nucleophilic) than pyridines, there is a greater influence on electrophilic additions, of substituents, especially those able to exert powerful mesomeric effects (Deady & Zoltewicz, 1971). Obviously, in a pyrazine, steric factors (Gallo, Roussel & Berg, 1988) always work against reaction at the N atom adjacent to a substituent; however, *N*-oxidation is believed to be less susceptible to steric effects than *N*-methylation (Grimmett & Keene, 1988; Dondoni, Modena & Todesco, 1961). *N*-Oxidation of 2-methylpyrazine produced 1- and 4-oxides in a ratio of 3:2 (Sato, 1978) and 2-ethoxy-3-methylpyrazine gave the 4-oxide (Klein, O'Donnell & Gordon, 1964).



(1a)  $R = H$   
(1b)  $R = Me$

For synthetic reasons we wished to prepare 2-methoxy-6-methylpyrazine 1-oxide; however, as the discussion above makes clear, we could not safely predict the regiochemistry for *N*-oxidation of 2-methoxy-6-methylpyrazine. Since *all* previous assignments of structure to *N*-oxidized simple pyrazines

have been based on chemical correlations and since there are certainly some regiochemically unexpected products encountered in pyrazine *N*-oxide chemistry [for example, pyrazine 1,4-dioxide gives 2,6-dichloropyrazine on reaction with phosphorous oxychloride (Klein, Hetman & O'Donnell, 1963)] we sought crystallographic confirmation for the structure of the product (1b) of *N*-oxidation of 2-methoxy-6-methylpyrazine. For comparison we also prepared and analysed a crystalline *N*-oxide (1a) from 2-methoxypyrazine.

**Experimental.** *N*-Oxidation of 2-methoxypyrazine and 2-methoxy-6-methylpyrazine (Bramwell & Wells, 1972; Lutz, Lazarus, Klutchko & Meltser, 1964) was effected efficiently by treatment with *m*-chloroperbenzoic acid in dichloromethane at room temperature giving (1a) and (1b) in isolated yields of 81 and 68% respectively. In each case formation of only one oxide was observed, as judged by TLC analysis. The same oxides were formed by oxidation with aqueous hydrogen peroxide/acetic acid.

Colourless prismatic crystals of (1a), m.p. 350–352 K (353–355 K; Okada, Kosasayama, Konno & Uchamaru, 1971) were obtained by recrystallization from ethyl acetate. After an intensity loss of 68% was found during data collection on a first sample, a second specimen, of approximate dimensions 0.100 × 0.300 × 0.300 mm, was coated with grease and mounted in a glass capillary for data collection on a Rigaku AFC-5R diffractometer with graphite-monochromated Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) using a 12 kW rotating-anode generator. Decay was still 31% but 1544 of the 3016 measurements yielded useful data. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 21 carefully centered reflexions in the range  $50.14 < 2\theta < 58.21^\circ$ . Data were collected at 293 (1) K using  $\omega/2\theta$  scan technique to a maximum  $2\theta$  value of  $120.2^\circ$ .  $\omega$  scans of several intense reflexions, made prior to data collection, had an average width at half height of  $0.27^\circ$  with a take-off angle of  $6.0^\circ$ . Scans of  $(0.94 + 0.30 \tan \theta)^\circ$  were made at a speed of  $32.0^\circ \text{ min}^{-1}$  (in  $\omega$ ). The weak reflexions [ $I < 10.0\sigma(I)$ ] were rescanned and the counts accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflexion. The ratio of peak counting time to background counting time was 2. The diameter of the incident-beam collimator was 0.5 mm and the crystal was 400.0 mm from the detector. Of the 3016 reflexions, 2861 were unique ( $R_{\text{int}} = 0.038$ ). Intensities of three representative reflexions, measured after every 150 reflexions, declined by 31.00%, so a linear correction factor was applied. The linear absorption coefficient for Cu  $K\alpha$  is  $9.1 \text{ cm}^{-1}$ . An empirical

Table 1. Positional and thermal parameters for *N*-oxide (1a) with e.s.d.'s in parentheses
$$B_{eq} = (8\pi^2/3)\sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
O1A	0.4867 (4)	0.6320 (3)	1.1313 (7)	5.9 (2)
O1B	0.4251 (4)	-0.1216 (3)	0.1035 (7)	6.1 (2)
O1C	0.2304 (4)	0.2735 (3)	0.4542 (7)	6.6 (2)
O1D	0.9069 (4)	0.2097 (3)	0.1460 (8)	7.3 (2)
O2A	0.1856 (4)	0.3695 (3)	0.9071 (7)	5.9 (2)
O2B	0.6865 (4)	0.1463 (4)	0.4551 (8)	5.9 (2)
O2C	0.4271 (4)	0.5831 (3)	0.6146 (7)	6.0 (2)
O2D	0.7143 (4)	-0.1004 (3)	0.0090 (7)	5.9 (2)
N1A	0.3785 (5)	0.5936 (4)	1.0544 (8)	4.5 (3)
N1B	0.5160 (5)	-0.0813 (4)	0.244 (1)	4.7 (3)
N1C	0.2326 (6)	0.3615 (4)	0.4518 (9)	5.1 (3)
N1D	0.9056 (6)	0.1225 (4)	0.1596 (9)	5.0 (3)
N2A	0.1442 (5)	0.5143 (4)	0.8841 (8)	4.9 (2)
N2B	0.7132 (5)	0.0044 (4)	0.5412 (8)	5.0 (3)
N2C	0.2347 (6)	0.5509 (4)	0.4443 (8)	4.8 (2)
N2D	0.9046 (6)	-0.0644 (4)	0.1775 (9)	5.0 (3)
C1A	0.1897 (7)	0.6071 (6)	0.922 (1)	5.2 (3)
C1B	0.6706 (7)	-0.0895 (6)	0.497 (1)	5.5 (3)
C1C	0.1398 (7)	0.4805 (6)	0.366 (1)	5.3 (3)
C1D	0.9983 (7)	0.0067 (6)	0.261 (1)	5.3 (3)
C2A	0.3024 (7)	0.6495 (4)	1.003 (1)	4.8 (3)
C2B	0.5748 (6)	-0.1334 (5)	0.353 (1)	4.6 (3)
C2C	0.1350 (6)	0.3884 (5)	0.367 (1)	5.2 (3)
C2D	1.0038 (6)	0.0991 (5)	0.253 (1)	5.5 (3)
C3A	0.3374 (6)	0.5014 (5)	1.019 (1)	4.3 (3)
C3B	0.5547 (7)	0.0130 (5)	0.280 (1)	4.7 (3)
C3C	0.3302 (7)	0.4293 (6)	0.538 (1)	4.8 (3)
C3D	0.8097 (6)	0.0554 (5)	0.076 (1)	4.6 (3)
C4A	0.2204 (7)	0.4634 (5)	0.935 (1)	4.3 (3)
C4B	0.6532 (6)	0.0527 (5)	0.429 (1)	4.0 (3)
C4C	0.3249 (7)	0.5213 (5)	0.525 (1)	4.9 (3)
C4D	0.8137 (7)	-0.0365 (5)	0.093 (1)	4.4 (3)
C5A	0.0649 (7)	0.3262 (6)	0.817 (1)	7.2 (4)
C5B	0.7916 (7)	0.1927 (5)	0.595 (1)	7.4 (4)
C5C	0.4314 (7)	0.6805 (5)	0.601 (1)	7.3 (4)
C5D	0.7141 (7)	-0.1973 (5)	0.020 (1)	6.6 (4)
H1A	0.1380	0.6469	0.8901	6.3
H1B	0.7105	-0.1278	0.5723	6.6
H1C	0.0709	0.4974	0.3045	6.4
H1D	1.0656	-0.0095	0.3314	6.4
H2A	0.3282	0.7161	1.0236	5.7
H2B	0.5496	-0.2001	0.3298	5.5
H2C	0.0647	0.3428	0.3107	6.3
H2D	1.0733	0.1456	0.3097	6.7
H3A	0.3881	0.4608	1.0518	5.1
H3B	0.5153	0.0515	0.2048	5.6
H3C	0.3991	0.4139	0.6038	5.8
H3D	0.7413	0.0706	0.0066	5.5
H51A	0.0178	0.3480	0.8973	8.6
H52A	0.0446	0.3425	0.6900	8.6
H53A	0.0532	0.2597	0.8059	8.6
H51B	0.7863	0.1791	0.7226	8.9
H52B	0.8547	0.1710	0.5594	8.9
H53B	0.8039	0.2587	0.5980	8.9
H51C	0.5064	0.7173	0.6668	8.7
H52C	0.4157	0.6876	0.4661	8.7
H53C	0.3750	0.7009	0.6612	8.7
H51D	0.6394	-0.2354	-0.0431	8.0
H52D	0.7700	-0.2159	-0.0445	8.0
H53D	0.7329	-0.2049	0.1543	8.0

Table 2. Positional and thermal parameters for *N*-oxide (1b) with e.s.d.'s in parentheses
$$B_{eq} = (8\pi^2/3)\sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
O1	0.5041 (2)	0.76059 (12)	-0.0063	6.1 (1)
O2	0.2396 (3)	0.44027 (13)	-0.005 (3)	5.1 (2)
N1	0.5088 (3)	0.6589 (1)	0.006 (4)	4.3 (2)
N2	0.5294 (3)	0.4416 (2)	-0.004 (4)	4.0 (2)
C1	0.6655 (4)	0.5033 (2)	0.004 (4)	3.6 (3)
C2	0.6599 (4)	0.6091 (2)	-0.010 (4)	4.0 (3)
C3	0.3690 (4)	0.6015 (2)	-0.016 (4)	3.4 (3)
C4	0.3872 (4)	0.4929 (2)	-0.007 (4)	4.3 (3)
C5	0.8327 (5)	0.4484 (5)	0.005 (4)	5.9 (4)
C6	0.2453 (5)	0.3262 (3)	-0.020 (4)	5.8 (4)
H2	0.760 (3)	0.657 (2)	-0.039 (11)	4.2
H3	0.263 (3)	0.644 (2)	0.038 (7)	4.4
H51	0.844 (7)	0.427 (5)	0.12 (2)	7.3
H52	0.828 (5)	0.383 (3)	-0.093 (11)	7.3
H53	0.930 (4)	0.500 (2)	-0.106 (7)	7.3
H61	0.140 (6)	0.300 (2)	0.075 (9)	5.5
H62	0.327 (6)	0.313 (3)	-0.173 (8)	5.5
H63	0.312 (5)	0.291 (2)	0.01 (3)	5.5

were obtained from a least-squares refinement using the setting angles of nine carefully centered reflexions in the range  $8 < 2\theta < 29^\circ$  corresponding to the orthorhombic cell. Data were collected at 294 (1) K using  $\omega/2\theta$  scan technique to a maximum  $2\theta$  value of  $49.9^\circ$ .  $\omega$  scans of several intense reflexions, made prior to data collection, had an average width at half height of  $0.30^\circ$  with a take-off angle of  $6.0^\circ$ . Scans of  $(0.60 + 0.35\tan\theta)^\circ$  were made at a speed of  $5.0^\circ \text{ min}^{-1}$  (in  $\omega$ ). The weak reflexions [ $I < 2.0\sigma(I)$ ] were rescanned (maximum total time 60 s) and the counts accumulated to assure good counting statistics. Moving-crystal moving-counter background measurements were made by scanning an additional 25% above and below the scan range. The ratio of peak counting time to background counting time was 2. The counter aperture was a variable horizontal slit with a width ranging from 2.0 to 6.0 mm and a vertical slit set to 4.0 mm. The diameter of the beam at the crystal was 1.3 mm and the crystal was 208 mm from the detector. While 1348 unique reflexions were collected, intensities of two representative reflexions, measured after every 150 reflexions, declined by 22.9%, so a linear drift correction was applied. The linear absorption coefficient for Mo  $K\alpha$  is  $1.0 \text{ cm}^{-1}$ . An empirical absorption correction, using the program *DIFABS* (Walker & Stuart, 1983) was applied and resulted in transmission factors ranging from 0.98 to 1.04. The data were corrected for Lorentz and polarization effects. The range of  $hkl$  was  $h - 9$  to 9,  $k - 15$  to 15 and  $l 0$  to 7.

The structures were solved by direct methods (Beurskens *et al.*, 1984; Gilmore, 1984). Non-H atoms were refined anisotropically. For (1a), H atoms were assigned to calculated positions then refined with C—H constrained to 0.95 Å. For (1b), H atoms were found by difference map and their positions refined. The final cycles of full-matrix least-squares refinement were based on 1544 observed

absorption correction, using the program *DIFABS* (Walker & Stuart, 1983) was applied and resulted in transmission factors ranging from 0.88 to 1.11. The range of  $hkl$  was  $h - 9$  to 13,  $k - 16$  to 16, and  $l - 7$  to 7.

A colourless tabular crystal of (1b), dimensions  $0.20 \times 0.22 \times 0.35 \text{ mm}$ , m.p. 403–405 K, obtained by recrystallization from ethyl acetate, was mounted on a glass fibre for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). Cell constants and an orientation matrix for data collection

reflexions for (1a) and 877 observed reflexions for (1b) with  $[I > 3.00\sigma(I)]$ , and 325 and 115 variable parameters for (1a) and (1b) respectively, and converged [largest parameter shift was 0.01 times its e.s.d. for (1a) and 0.16 times its e.s.d. for (1b)] with unweighted and weighted factors of  $R = 0.061$  and  $0.032$  for (1a) and (1b), and  $wR = 0.075$  and  $0.027$  for (1a) and (1b), respectively.

Standard deviations,  $S$ , of observations of unit weight were 2.26 for (1a) and 2.12 for (1b). The weighting scheme was based on counting statistics and included a factor ( $p = 0.03$ ) to downweight the intense reflexions. Plots of  $\sum w(|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflexion order in data collection,  $\sin\theta/\lambda$ , and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.18 and  $-0.21 \text{ e \AA}^{-3}$ , and 0.15 and  $-0.14 \text{ e \AA}^{-3}$ , respectively, for (1a) and (1b).

All calculations were performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985). Neutral-atom scattering factors were taken from Cromer & Waber (1974), anomalous-dispersion effects were included in

$F_c$  (Ibers & Hamilton, 1964), and the values of  $\Delta f'$  and  $\Delta f''$  were those of Cromer & Waber (1974).

**Discussion.** The atomic parameters for 3-methoxy-pyrazine 1-oxide (1a) and 3-methoxy-5-methyl-pyrazine 1-oxide (1b) are listed in Tables 1 and 2;\* Figs. 1 and 2 show *PLUTO* (Motherwell & Clegg, 1978) drawings of the molecules and the numbering systems used in Tables 1 and 2. Each *N*-oxide, (1a) and (1b), is essentially planar, the methoxyl methyl groups lying in the plane of the heterocyclic rings oriented away from the *ortho* H atom *i.e.* close to the *N*-atom lone pair. In the case of (1b) *z/c* is close to zero; the small departures from planarity justify the choice of space group *Pna2*, rather than the higher symmetry *Pnma* which would require the molecule to lie on a plane of symmetry at  $y/b = 0.25$ ; an independent check refinement in this second space group proved to give a worse fit. The *N*-oxide bond lengths of 1.294 and 1.297 Å found here compare well with *N*—O bond lengths (in the range 1.294–1.309 Å) of the only two pyrazine-containing *N*-oxides for which data is available from the Cambridge Structural Database, even though one of these is a quinoxaline and one a phenazine and each is a bis-1,4-di-*N*-oxide.

The chemical results seem best interpreted as confirming a deactivating influence, presumably a combination of steric and  $-I$  mesomeric, of methoxyl on electrophilic addition at an adjacent azine N atom. The additional methyl, in 2-methoxy-6-methylpyrazine, aggravates the steric aspect while contributing only a little, inductively, to nucleophilic reactivity at the adjacent N atom.

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\* Lists of structure factors, anisotropic thermal parameters, bond distances and angles, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54536 (54 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0025]

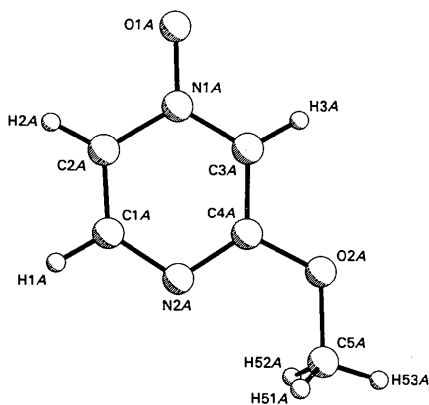


Fig. 1. *PLUTO* drawing of *N*-oxide (1a), showing the atom-numbering scheme.

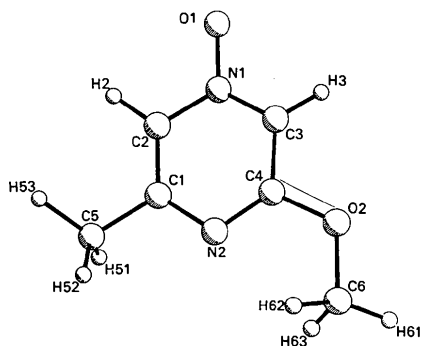


Fig. 2. *PLUTO* drawing of *N*-oxide (1b), showing the atom-numbering scheme.

## References

- BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., GOULD, R. O., VAN DER HARK, TH. E. M., PRICK, P. A., NOORDIK, J. H., BEURSKENS, G., PARTHASARATHI, V., BRUINS SLOT, H. J., HALTIWANGER, R. C., STRUMPEL, M. & SMITS, J. M. M. (1984). *DIRDIF*. Tech. Rep. 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- BRAMWELL, A. F. & WELLS, R. D. (1972). *Tetrahedron*, **28**, 4155–4170.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DEADY, L. W. & ZOLTEWICZ, J. A. (1971). *J. Am. Chem. Soc.* **93**, 5475–5477.

- DONDONI, A., MODENA, G. & TODESCO, P. E. (1961). *Gazz. Chim. Ital.* **91**, 613–619.
- GALLO, R., ROUSSEL, C. & BERG, U. (1988). *Adv. Heterocycl. Chem.* **43**, 173–299.
- GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- GRIMMETT, M. R. & KEENE, B. R. T. (1988). *Adv. Heterocycl. Chem.* **43**, 127–171.
- IBERS, J. A. & HAMILTON, W. C. (1964). *Acta Cryst.* **17**, 781–782.
- JOVANOVIĆ, M. V. (1985). *Heterocycles*, **23**, 2299–2315.
- KATRITZKY, A. R. (1963). Editor. *Physical Methods in Heterocyclic Chemistry*, Vol. I. New York, London: Academic Press.
- KLEIN, B., HETMAN, N. E. & O'DONNELL, M. E. (1963). *J. Org. Chem.* **28**, 1682–1686.
- KLEIN, B., O'DONNELL, M. E. & GORDON, J. M. (1964). *J. Org. Chem.* **29**, 2623–2626.
- LUTZ, W. B., LAZARUS, S., KLUTCHKO, S. & MELTNER, R. I. (1964). *J. Org. Chem.* **29**, 415.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- OKADA, S., KOSASAYAMA, A., KONNO, T. & UCHIMARU, F. (1971). *Chem. Pharm. Bull.* **19**, 1344–1357.
- SATO, N. (1978). *J. Org. Chem.* **43**, 3367–3370.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1992). **C48**, 311–315

## Structure of 2,8-Dithia[9](9,10)anthracenophane

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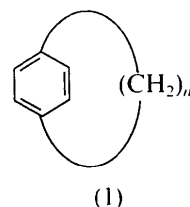
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**Abstract.**  $C_{21}H_{22}S_2$ ,  $M_r = 338.64$ , monoclinic,  $P2_1/n$ ,  $a = 9.140$  (4),  $b = 25.926$  (15),  $c = 14.481$  (9) Å,  $\beta = 93.55$  (4)°,  $V = 3428.4$  Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.29$ ,  $D_x = 1.312$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.261$  mm<sup>-1</sup>,  $F(000) = 1440$ ,  $T = 295$  K,  $R = 0.0432$  for 3673 unique observed reflections. This represents the first crystal structure determination of an [n](9,10)anthracenophane. The two molecules in the asymmetric unit are nearly identical, have approximate  $C_2$  symmetry and exhibit less-severe aryl ring distortion than predicted by molecular-mechanics calculations. The results of a comparison of selected angles in this structure with two other reported thiacyclophanes permits the strain in these molecules to be inferred.

**Introduction.** The current detailed picture of [n]paracyclophane (1) structure has evolved through more than 30 years of determined effort to prepare and characterize members of this family with shorter bridge lengths and correspondingly greater aryl ring distortion (Rosenfeld & Choe, 1983). That history is characterized by a wonderful interplay of computational chemistry and experimental structural probes, particularly NMR spectroscopy (Mitchell, 1983) and X-ray crystal structure determination

(Rosenfeld & Choe, 1983). This pattern, unfortunately, has not been repeated for benzologous systems though their structure and chemistry promise to be rich and decidedly different than the [n]paracyclophanes.



The smallest known [n](9,10)anthracenophane with a saturated aliphatic bridge has  $n = 10$  (Vögtle & Koo Tze Mew, 1978). However, 3,5-diketo[8](9,10)anthracenophane (Wynberg & Helder, 1971; Rosenfeld & Sanford, 1987) and 2,7-dithia[8](9,10)anthracenophane (2) (Chung & Rosenfeld, 1983) have been reported and both undergo air oxidation on standing in solution at room temperature. This enhanced reactivity is presumably a result of bending of the central ring of the anthracene moiety and molecular-mechanics modeling suggests that (2)–(4) have central rings that are *more* distorted than the aryl rings of [n]paracyclophanes of corresponding  $n$  despite the substantially longer C—S bonds in the

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