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References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. *World List of Crystallographic Computer Programs*, 2nd ed., Appendix, p. 52. Utrecht: Oosthoek.
- BRISSE, F. & PÉREZ, S. (1976). *Acta Cryst.* B32, 2110–2115.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* 18, 104–109.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York.
- PÉREZ, S. & BRISSE, F. (1975). *Canad. J. Chem.* 53, 3551–3556.
- PÉREZ, S. & BRISSE, F. (1976a). *Acta Cryst.* B32, 470–474.
- PÉREZ, S. & BRISSE, F. (1976b). *Acta Cryst.* B32, 1518–1521.
- PÉREZ, S. & BRISSE, F. (1977). *Acta Cryst.* B33, 1673–1677.
- POULIN-DANDURAND, S., PÉREZ, S. & BRISSE, F. (1977). To be published.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
- VOGEL, A. I. (1962). *Practical Organic Chemistry*, 3rd ed., p. 268. London: Longmans.

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trans-6a, 11b-Dihydro-5-methylbenzo[*b*]thieno[2,3-*c*]quinolin-6-one (I) and *cis*-6a, 11b-Dihydrobenzo[*b*]thieno[2,3-*c*]quinolin-6-one 7,7-Dioxide (II)

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Abstract. (I): C₁₆H₁₃NSO, monoclinic, *P*2₁/*a*, *a* = 10.258 (6), *b* = 14.518 (9), *c* = 8.898 (5) Å, β = 104.9 (2)°, *Z* = 4, *d*_x = 1.39 g cm⁻³, μ*R*_{max} = 5.7. The structure was solved by the symbolic addition procedure. The tetracyclic ring system is *trans*. (II): C₁₅H₁₁NSO₃, triclinic, *P*1̄, *a* = 8.300 (4), *b* = 10.768 (8), *c* = 7.957 (4) Å, α = 110.2 (1), β = 73.7 (1), γ = 100.8 (1)°, *Z* = 2, *d*_x = 1.49 g cm⁻³, μ*R*_{max} = 8.2. The structure was solved by the heavy-atom method. The tetracyclic ring system is *cis*.

Introduction. Heterocyclic analides, such as benzo[*b*]thiophene, undergo photocyclization in the presence of dissolved oxygen to yield heterocyclic

condensed quinolines (Kanaoka, Itoh, Hatanaka, Flippen, Karle & Witkop, 1975). X-ray analyses were performed on two of these quinolines to determine the stereoconfiguration of the ring fusion.

Both crystals were obtained through B. Witkop of NIAMD. Data for both compounds were collected on an automatic computer-controlled diffractometer (Cu *K*α, λ = 1.54178 Å, Ni filter) using the θ–2θ scan technique. The crystal of (I) (~0.55 × 0.58 × 0.19 mm) gave 2074 independent reflections out to a 2θ_{max} of 126.5° and the crystal of (II) (~0.13 × 0.38 × 0.68 mm) yielded 1574 reflections.

The structure of (I) was solved by the symbolic addition procedure for centrosymmetric molecules (Karle & Karle, 1966). For molecule II, the S atom was located in a Patterson map and the remaining atoms were found in two cycles of difference Fourier maps. Full-matrix least-squares refinement (Busing *et al.*, 1971) was carried out on both molecules. The atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962). The function minimized was Σ *w*(|*F*_o| – |*F*_c|)², where the weights *w* (derived from estimated standard deviations of observed intensity) were calculated

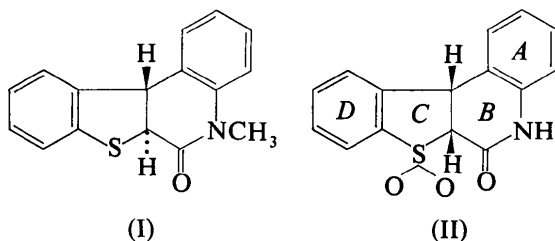


Table 1. *Fractional coordinates*

Molecule I				Molecule II			
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.1654	0.4459	0.2828	C(1)	0.2561	0.3705	0.6491
C(2)	0.0399	0.4799	0.2745	C(2)	0.1787	0.4848	0.7601
C(3)	-0.0060	0.5597	0.1952	C(3)	0.1645	0.5792	0.6844
C(4)	0.0809	0.6090	0.1272	C(4)	0.2329	0.5612	0.4988
N(5)	0.2993	0.6262	0.0664	N(5)	0.3895	0.4395	0.2044
C(6)	0.4324	0.6199	0.1152	C(6)	0.4575	0.3328	0.0760
S(7)	0.6550	0.5200	0.2833	S(7)	0.2614	0.0993	0.0589
C(8)	0.7138	0.3632	0.4703	C(8)	0.1300	-0.0957	0.2308
C(9)	0.6695	0.2824	0.5296	C(9)	0.1233	-0.1443	0.3724
C(10)	0.5384	0.2575	0.4840	C(10)	0.2118	-0.0739	0.5065
C(11)	0.4391	0.3128	0.3853	C(11)	0.3063	0.0458	0.5041
C(12)	0.4824	0.3945	0.3291	C(12)	0.3131	0.0972	0.3641
C(13)	0.6139	0.4187	0.3710	C(13)	0.2251	0.0241	0.2307
C(14)	0.4829	0.5526	0.2462	C(14)	0.4398	0.2095	0.1327
C(15)	0.3921	0.4638	0.2157	C(15)	0.4108	0.2267	0.3392
C(16)	0.2549	0.4926	0.2145	C(16)	0.3220	0.3498	0.4620
C(17)	0.2079	0.5762	0.1346	C(17)	0.3135	0.4488	0.3892
C(18)	0.2403	0.6956	-0.0552	C(19)	0.5285	0.3301	-0.0837
O(19)	0.5131	0.6660	0.0640	O(20)	0.3167	0.0043	-0.1198
				O(21)	0.1270	0.1752	0.0841
Standard deviation (average)*							
	0.0006	0.0004	0.0007		0.0003	0.0002	0.0003

* Standard deviations are those indicated by the least-squares results.

Table 2. *Difference-map coordinates for the hydrogen atoms*

Molecule I				Molecule II			
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
HC(1)	0.189	0.383	0.334	HC(1)	0.262	0.298	0.707
HC(2)	-0.041	0.453	0.315	HC(2)	0.139	0.501	0.890
HC(3)	-0.083	0.598	0.209	HC(3)	0.100	0.651	0.763
HC(4)	0.027	0.664	0.068	HC(4)	0.227	0.625	0.452
HC(8)	0.805	0.386	0.499	HN(5)	0.399	0.508	0.175
HC(9)	0.750	0.241	0.577	HC(8)	0.067	-0.144	0.122
HC(10)	0.498	0.200	0.535	HC(9)	0.055	-0.220	0.391
HC(11)	0.340	0.295	0.356	HC(10)	0.209	-0.105	0.584
HC(14)	0.468	0.587	0.354	HC(11)	0.365	0.088	0.599
HC(15)	0.386	0.433	0.097	HC(14)	0.538	0.162	0.070
HC(18)	0.141	0.671	0.836	HC(15)	0.518	0.237	0.363
HC(18)'	0.186	0.747	-0.007				
HC(18)''	0.306	0.706	0.885				

according to Gilardi (1973). In addition, for compound I, all data with $|F_o| < 3.0\sigma_{|F_o|}$ were given zero weight and omitted from the refinement. For (II) all data were used in the refinement. No absorption corrections were applied. All the H atoms for both molecules were located in difference maps and included in the least-squares refinement as constants. The refinement of (I) was terminated arbitrarily at an earlier stage of convergence than that of (II). When refinement was complete the standard deviation of an observation of unit weight was 8.7 for (I) and 3.4 for (II). Final *R* factors for molecule I were *R* = 9.2% (*R_w* = 14.4%)

for the data used in the refinement and *R* = 9.7% (*R_w* = 14.4%) for the full set of data. For (II) the final *R* factors were *R* = 4.2% and *R_w* = 5.3%. Refined coordinates for the nonhydrogen atoms are listed in Table 1. Difference-map coordinates for the H atoms are listed in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32788 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

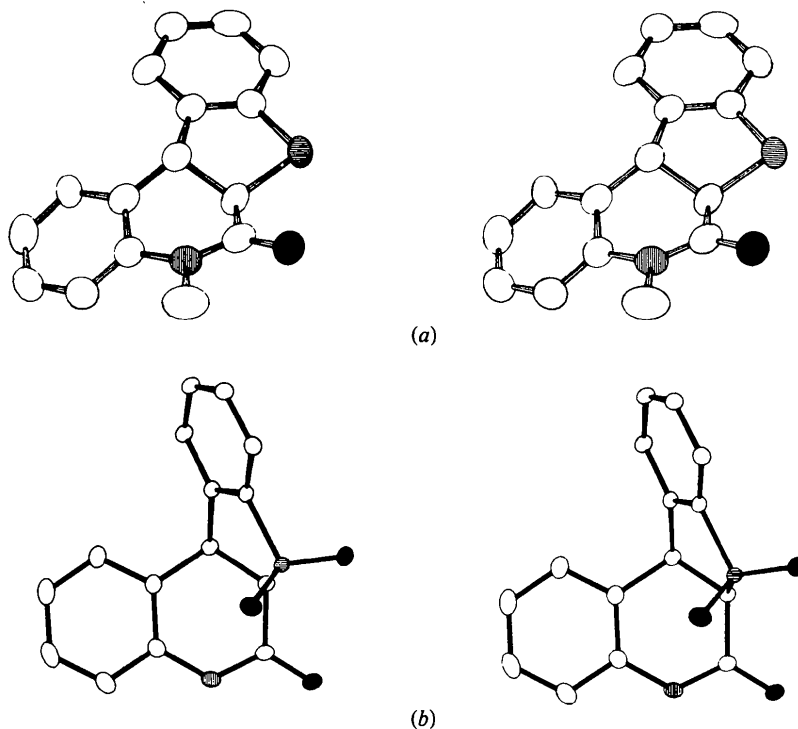


Fig. 1. (a) Stereodiagram of molecule I. (b) Stereodiagram of molecule II. In both cases the S atom is horizontally shaded, the N atom is vertically shaded and the O atoms are completely shaded. The figures were drawn by a computer using the program ORTEP (Johnson, 1965).

Discussion. The stereoconfiguration of both molecules is illustrated in Fig. 1. Bond distances and angles are illustrated in Figs. 2 and 3 for molecules I and II respectively. The effects of conjugation of the aromatic rings and the C=O group in both molecules can be seen by the shortened bond lengths of the adjacent N—C, C—C, and S—C single bonds. In the aromatic rings (*A* and *D*) the average C—C—C angle is 120.0° for (I) and 120.1° for (II). The C—S—C angle is 87.8° in (I) and

93.4° in (II). Differences between the molecules, which have an effect on their structures, are the configuration of the H atoms on C(14) and C(15) and the bonding environment of the N atom. In (I) the H atoms are *trans* to each other, which allows the molecule to be fully extended with all the ring junctions (*A/B*, *B/C*, and *C/D*) *trans*. The effect of the repulsive forces between the H atoms on C(1) and C(11) can be seen in

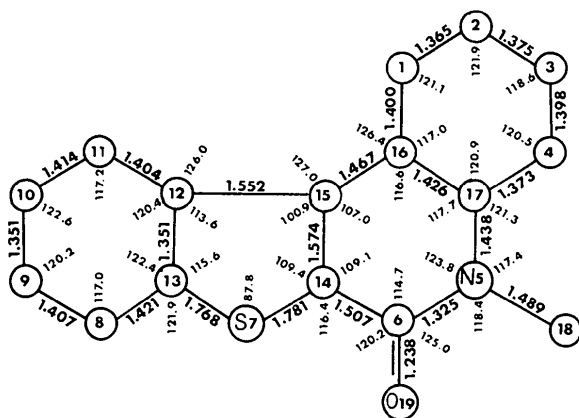


Fig. 2. Bond distances (Å) and angles (°) for molecule I. Standard deviations are of the order of 0.010 Å for the distances and 0.6° for the angles.

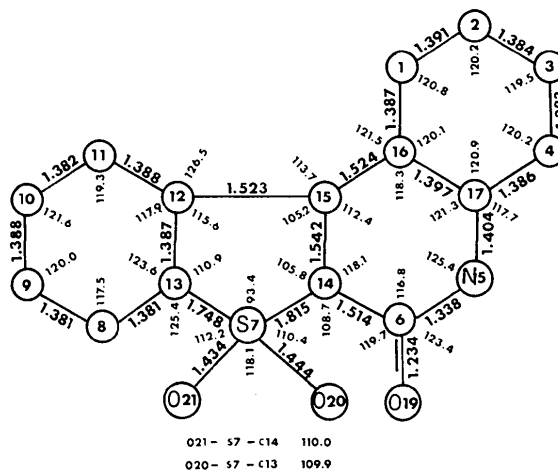


Fig. 3. Bond lengths (Å) and angles (°) for molecule II. Standard deviations are of the order of 0.003 Å for the bond lengths and 0.3° for the angles.

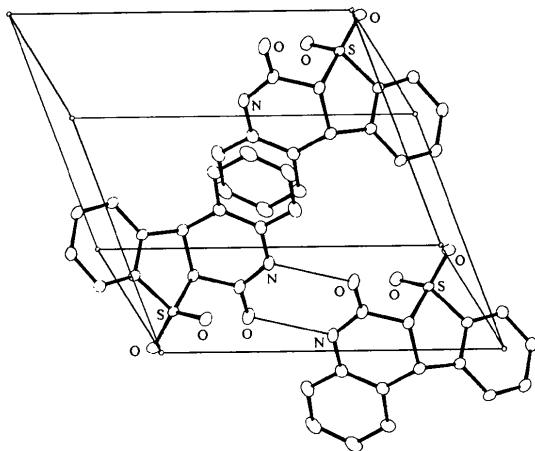


Fig. 4. Packing diagram for molecule II illustrating the NH...O hydrogen bond.

the large values for the external C—C—C angles at the three-connected C atoms, *i.e.* C(12), C(15) and C(16): 126.0, 127.0 and 126.4°, respectively. In (II) the angular tertiary H atoms on C(14) and C(15) are *cis* to each other and consequently there is a *cis* junction between rings B and C which gives the molecule a folded rather than an extended conformation. As a consequence, the H atoms on C(1) and C(11) do not interfere with each other and the values for the external angles at C(15) and C(16) (113.7 and 121.5°, respectively) are smaller than the related angles in (I). For molecule I the average C—H distance is 1.05 Å. In (II) the N—H distance is 0.84 Å and the average C—H

distance is 0.95 Å. Angles involving the H atoms fall within normal ranges for both molecules.

The change in the environment at the N atom, from a CH₃ group in (I) to a H atom in (II), has an effect on the molecular packing. The methyl substituent in (I) precludes the possibility of any hydrogen bonding, and the molecules are held together in the unit cell solely by van der Waals forces, with the closest intermolecular approaches being C(8)...C(16) at 3.47 Å and C(11)...C(18) at 3.48 Å. In (II) the molecules are held together in pairs across a center of symmetry by a hydrogen bond extending from the imido group to the O of the lactam carbonyl, with an N...O distance of 2.86 Å and an NH...O angle of 168.7° (see Fig. 4). This hydrogen bond allows the molecules to pack more closely in the unit cell and accounts in part for the higher crystal density noted for (II).

References

- BUSING, W. R., MARTIN, K. O., LEVY, H. A., ELLISON, R. D., HAMILTON, W. C., IBERS, J. A., JOHNSON, C. K. & THIESSEN, W. E. (1971). *ORXFLS3*. Oak Ridge National Laboratory, Tennessee.
- GILARDI, R. D. (1973). *Acta Cryst.* B29, 2089–2095.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KANAOKA, Y., ITOH, K., HATANAKA, Y., FLIPPEN, J. L., KARLE, I. L. & WITKOP, B. (1975). *J. Org. Chem.* 40, 3001–3003.
- KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* 21, 849–859.

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Dehydrated Natural Erionite with Stacking Faults of the Offretite Type

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Abstract. A single crystal of erionite, $\sim\text{Mg}_{0.7}\text{Na}_{0.9}\text{K}_{2.0}\text{Ca}_{2.4}\text{Al}_{9.1}\text{Si}_{26.9}\text{O}_{72} \cdot x\text{H}_2\text{O}$, from Mazé, Japan, was dehydrated in high vacuum at 300°C for 1 d, and the structure refined in $P6_3/mmc$ [$a = 13.252$ (4), $c = 14.810$ (7) Å] to a weighted R of 0.062. About 6% of the single six-membered rings are stacked AAB as in offretite instead of the $AABAAC$ stacking of erionite. In dehydrated erionite the center of the cancrinite cage is occupied by Ca with trigonal-prismatic coordination instead of K as in the hydrated

variety. This internal ion-exchange during dehydration results in K moving to a planar six-coordinated site at the center of an eight-membered ring. The Na, Mg and remaining Ca ions are bonded to three O atoms in the single six-membered rings at the ends of the erionite cages. The unusually long Ca—O distance of 2.73 Å may result from forces resisting further collapse of the cancrinite cage. Si,Al disorder is indicated by the near equality of the mean T —O distances for the two independent tetrahedra. The deviation of an individual