Fujii, S. (1979). *MOLCON. The Universal Crystallographic Computing System–Osaka.* The Computation Center, Osaka Univ., Japan.

Harkema, S., van Hummel, G. J. & Gaymans, R. J. (1980). *Acta Cryst.* B36, 3182–3184.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Jagannathan, N. R., Subramanian, E., Srinivasan, R. & Trotter, J. (1984). *Acta Cryst.* C40, 1743–1744.

Johnson, C. K. (1971). *ORTEP.* Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Kashino, S., Sasaki, M. & Haisa, M. (1973). *Bull. Chem. Soc. Jpn*, 46, 1375–1379.

Main, P., Germain, G. & Woolfson, M. M. (1984). *MULTAN84. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Morgan, P. W. & Kwolek, S. L. (1975). *Macromolecules*, 8, 104–111.

Moritani, Y., Sasahara, N., Kashino, S. & Haisa, M. (1987). *Acta Cryst.* C43, 154–158.

Müller, U. (1978). *Acta Cryst.* B34, 1044–1046.

Pineault, C. & Brisse, F. (1983*a*). *Acta Cryst.* C39, 1434–1437.

Pineault, C. & Brisse, F. (1983*b*). *Acta Cryst.* C39, 1437–1439.

Takusagawa, F., Hirotsu, K. & Shimada, A. (1971). *Bull. Chem. Soc. Jpn*, 44, 1274–1278.

Yao, J. (1981). *Acta Cryst.* A37, 642–644.

Acta Cryst. (1990). C46, 849–852

Structure of 6-Methoxy-1-[(4-methoxyphenyl)amino]xanthen-9-one

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Abstract. $C_{21}H_{17}NO_4$, $M_r = 347{\cdot}37$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}060\,(2)$, $b = 14{\cdot}024\,(4)$, $c = 34{\cdot}005\,(10)$ Å, $V = 3366{\cdot}8$ Å^3, $Z = 8$ (two molecules per asymmetric unit), $D_x = 1{\cdot}37$, $D_m = 1{\cdot}332$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}69$ mm^{-1}, $F(000) = 1456$, $T = 293$ K, $R = 0{\cdot}036$, $wR = 0{\cdot}034$ for 1925 reflections with $I > 3\sigma(I)$. The pyran ring in both molecules is in a boat conformation. There is an internal hydrogen bond N—H···O linking the nitrogen of the 4-methoxy-*N*-substituted aniline and the carbonyl oxygen of the pyranoid ring in each molecule.

Introduction. Xanthone derivatives have been well documented as biogenic precursors (Vinod & Gupta, 1979) and neuroleptic (Lassen, Bogeso, Hansen, Buss & Bigler, 1980) and antiallergic (Pfister, 1980) agents. The title compound is a condensation product obtained by treating 2-bromo-6-methoxycoumaran-3-one with a 4-substituted aromatic amine (Chandrasekhar & Ramadas, unpublished) in glacial acetic acid medium. The crystal structure analysis of this condensation product was undertaken in order to confirm the assigned structure.

Experimental. Pale pink prismatic single crystals were grown by slow evaporation of the compound in hexane. The density was measured by flotation. Intensity data from a crystal of approximate dimensions $0{\cdot}40 \times 0{\cdot}45 \times 0{\cdot}66$ mm were collected up to $(\sin\theta/\lambda) = 0{\cdot}63$ Å^{-1} with ω–2θ scan using Ni-filtered Cu $K\alpha$ radiation on an Enraf–Nonius CAD-4 diffractometer. Cell parameters were refined by least-squares calculations from 20 reflections with $35 < \theta < 45°$. Two strong reflections ($2\bar{2}\bar{9}$, $2\bar{4}\bar{6}$) monitored periodically during data collection showed that the crystal was stable. Index range of unique data $0 \le h \le 7$, $0 \le k \le 15$, $0 \le l \le 37$. 2995 reflections were collected of which 1925 unique reflections with $I > 3\sigma(I)$ were considered observed. $R_{\mathrm{int}} = 0{\cdot}000$, $R_{\mathrm{sigma}} = 0{\cdot}0214$. Lp correction applied, absorption and extinction neglected.

Structure solution by multi-solution technique using *SHELXS*86 (Sheldrick, 1986). Refinement on *F* by least-squares method with *SHELX*76 (Sheldrick, 1976). H-atom positions from difference Fourier maps at intermediate stages. Final refinement with non-H atoms anisotropic and H atoms isotropic converged to $R = 0{\cdot}036$ and $wR = 0{\cdot}034$ with $w = K\{[\sigma(F_o)]^2 + g(|F_o|)^2\}^{-1}$, where $K = 4{\cdot}5716$ and $g = 0{\cdot}000064$. Quantity minimized was $\sum w(|F_o| - K|F_c|)^2$. $(\mathrm{Shift/e.s.d.})_{\max} = 0{\cdot}019$. Maximum and minimum heights in final difference synthesis were $0{\cdot}13$ and $-0{\cdot}21$ e Å^{-3}. Atomic scattering factors were from *SHELX*76 and all calculations were performed using a Siemens 7580-E computer.

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Discussion. The final atomic coordinates are listed in Table 1,* and a perspective view of the two molecules (A and B) in the asymmetric unit is shown in Fig. 1. The xanthene groups of the two molecules in the asymmetric unit are related by a pseudo centre of inversion. Bond lengths, bond angles and selected torsion angles involving only the non-H atoms are given in Table 2. Fig. 2 is a packing diagram of the molecules.

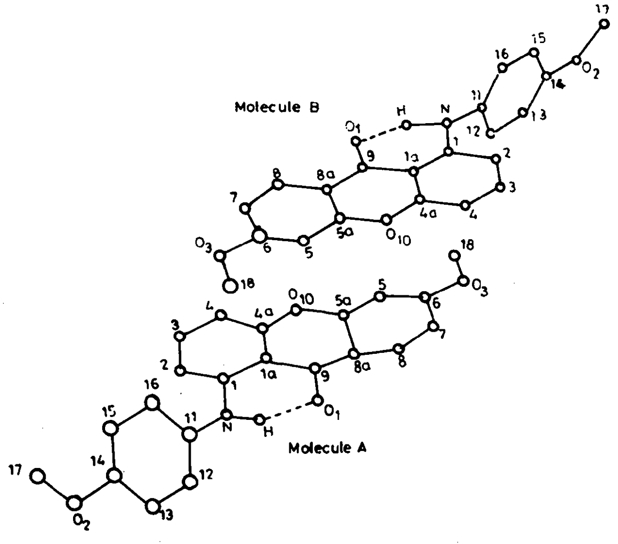

Fig. 1. Perspective view of the molecules.

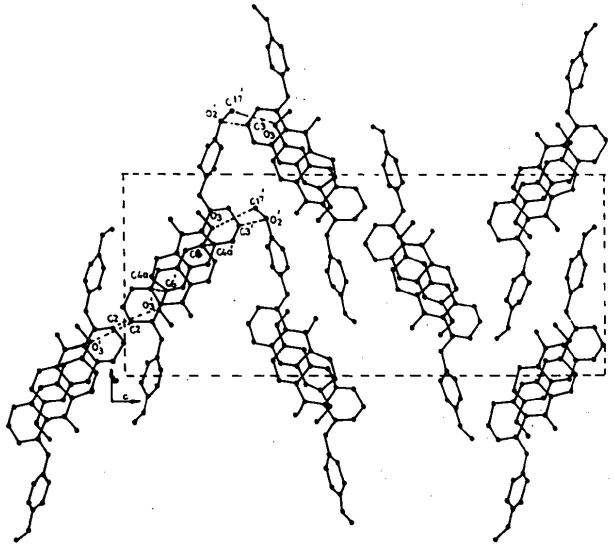

Fig. 2. Packing of molecules in a unit cell.

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}
Molecule A				
C(1)	6772 (6)	2569 (3)	609 (1)	44 (3)
C(1a)	6863 (6)	3472 (2)	804 (1)	40 (2)
C(2)	6279 (6)	2540 (3)	212 (1)	50 (3)
C(3)	5849 (7)	3365 (3)	14 (1)	54 (3)
C(4)	5915 (6)	4248 (3)	194 (1)	47 (3)
C(4a)	6450 (6)	4282 (3)	582 (1)	43 (3)
C(5)	6927 (6)	6243 (3)	1257 (1)	43 (3)
C(5a)	6911 (6)	5304 (3)	1130 (1)	41 (2)
C(6)	7276 (6)	6397 (3)	1648 (1)	46 (3)
C(7)	7585 (6)	5636 (3)	1911 (1)	52 (3)
C(8)	7593 (6)	4731 (3)	1770 (1)	50 (3)
C(8a)	7259 (6)	4534 (3)	1373 (1)	40 (2)
C(9)	7321 (6)	3573 (3)	1219 (1)	42 (3)
C(11)	6998 (7)	804 (3)	697 (1)	50 (3)
C(12)	8442 (6)	165 (3)	769 (1)	54 (3)
C(13)	8247 (7)	−785 (3)	672 (1)	62 (3)
C(14)	6588 (8)	−1118 (3)	501 (1)	54 (3)
C(15)	5150 (7)	−490 (3)	427 (1)	58 (3)
C(16)	5345 (7)	462 (3)	529 (1)	60 (3)
C(17)	4942 (8)	−2456 (3)	239 (2)	82 (4)
C(18)	7201 (7)	8091 (3)	1564 (1)	66 (3)
N	7241 (5)	1767 (2)	818 (1)	53 (2)
O(1)	7748 (4)	2891 (2)	1435 (1)	52 (2)
O(2)	6562 (5)	−2068 (2)	425 (1)	80 (2)
O(3)	7359 (4)	7276 (2)	1817 (1)	61 (2)
O(10)	6513 (4)	5184 (2)	739 (1)	45 (2)
Molecule B				
C(1)	2383 (6)	8147 (3)	1805 (1)	47 (3)
C(1a)	2286 (5)	7212 (3)	1639 (1)	39 (2)
C(2)	2802 (7)	8241 (3)	2203 (1)	52 (3)
C(3)	3092 (7)	7455 (3)	2434 (1)	55 (3)
C(4)	3007 (7)	6531 (3)	2285 (1)	51 (3)
C(4a)	2610 (6)	6432 (3)	1891 (1)	44 (3)
C(5)	2225 (6)	4369 (3)	1265 (1)	42 (2)
C(5a)	2213 (5)	5325 (3)	1367 (1)	40 (2)
C(6)	1816 (6)	4143 (3)	881 (1)	45 (3)
C(7)	1417 (6)	4849 (3)	604 (1)	51 (3)
C(8)	1436 (6)	5782 (3)	715 (1)	50 (3)
C(8a)	1851 (6)	6051 (3)	1104 (1)	40 (2)
C(9)	1904 (5)	7035 (3)	1226 (1)	43 (3)
C(11)	2342 (7)	9872 (3)	1697 (1)	53 (3)
C(12)	4006 (7)	10351 (3)	1615 (1)	56 (3)
C(13)	4236 (7)	11276 (3)	1730 (1)	58 (3)
C(14)	2801 (7)	11750 (3)	1930 (1)	51 (3)
C(15)	1142 (7)	11268 (3)	2018 (1)	64 (3)
C(16)	920 (7)	10336 (3)	1897 (1)	64 (3)
C(17)	1804 (9)	13189 (3)	2249 (1)	85 (4)
C(18)	2195 (7)	2484 (3)	1012 (1)	55 (3)
N	2101 (6)	8911 (2)	1566 (1)	57 (2)
O(1)	1649 (5)	7695 (2)	986 (1)	60 (2)
O(2)	3134 (5)	12684 (2)	2017 (1)	67 (2)
O(3)	1751 (4)	3231 (2)	741 (1)	54 (2)
O(10)	2592 (4)	5509 (2)	1757 (1)	45 (2)

Xanthen-9-one group. Both the rings fused to the pyran ring of the xanthenone group are aromatic, as seen from their average C—C bond lengths and their C—C—C bond angles. In molecule A both deviate by small, yet significant, amounts from planarity, assuming distorted boat conformations, but in molecule B they do not. The asymmetry parameters of the distorted rings are $\Delta C_s(4a) = 0{\cdot}4\ (6)$ and $\Delta C_s(5a) = 0{\cdot}7\ (6)°$.

The average values of the two C—O bond lengths in the pyran ring, namely 1·371 (4) Å in molecule A and 1·375 (4) Å in molecule B, agree well with the values reported for this bond in 9-isopropylxanthene [1·364 (7) Å] (Chu & Yang, 1977), hexachloroxanthene [1·379 (9) Å] (Soderholm, Sonnerstam,

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms, selected torsion angles, intermolecular contacts below 3·5 Å and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52534 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *bond angles* (°), *hydrogen-bond parameters* (Å *and* °) *and torsion angles* (°) *with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*
C(18)—O(3)	1·435 (5)	1·430 (5)
O(3)—C(6)	1·361 (5)	1·365 (5)
C(6)—C(5)	1·369 (6)	1·375 (5)
C(6)—C(7)	1·410 (6)	1·393 (6)
C(7)—C(8)	1·357 (6)	1·361 (6)
C(8)—C(8*a*)	1·397 (5)	1·408 (6)
C(8*a*)—C(5*a*)	1·383 (5)	1·378 (5)
C(5)—C(5*a*)	1·386 (5)	1·385 (5)
C(5*a*)—O(10)	1·369 (4)	1·376 (4)
O(10)—C(4*a*)	1·374 (4)	1·374 (5)
C(4*a*)—C(1*a*)	1·392 (5)	1·408 (5)
C(9)—C(1*a*)	1·456 (6)	1·451 (5)
C(8*a*)—C(9)	1·447 (5)	1·441 (5)
O(1)—C(9)	1·244 (5)	1·247 (5)
C(4*a*)—C(4)	1·376 (6)	1·375 (5)
C(4)—C(3)	1·381 (6)	1·392 (6)
O(2)—C(3)	1·373 (6)	1·369 (6)
C(2)—C(1)	1·394 (6)	1·391 (6)
C(1*a*)—C(1)	1·432 (5)	1·429 (5)
C(1)—N	1·371 (5)	1·361 (5)
N—C(11)	1·422 (5)	1·430 (5)
C(11)—C(12)	1·379 (6)	1·381 (7)
C(12)—C(13)	1·379 (6)	1·366 (6)
C(13)—C(14)	1·387 (7)	1·389 (6)
C(14)—C(15)	1·367 (7)	1·385 (7)
C(15)—C(16)	1·386 (6)	1·380 (6)
C(16)—C(11)	1·385 (7)	1·376 (7)
C(14)—O(2)	1·359 (5)	1·363 (5)
O(2)—C(17)	1·415 (7)	1·416 (6)
C(18)—O(3)—C(6)	117·7 (3)	117·1 (3)
O(3)—C(6)—C(7)	114·2 (3)	115·1 (3)
O(3)—C(6)—C(5)	124·1 (3)	123·6 (3)
C(6)—C(7)—C(8)	118·9 (4)	119·6 (4)
C(7)—C(8)—C(8*a*)	121·7 (4)	121·3 (4)
C(8)—C(8*a*)—C(5*a*)	117·0 (3)	116·8 (3)
C(8*a*)—C(5*a*)—C(5)	123·6 (3)	123·6 (3)
C(5*a*)—C(5)—C(6)	117·0 (3)	117·4 (3)
C(5)—C(6)—C(7)	121·7 (4)	121·3 (4)
C(5)—C(5*a*)—O(10)	114·9 (3)	114·9 (3)
C(8)—C(8*a*)—C(9)	122·0 (3)	122·2 (2)
C(5*a*)—C(8*a*)—C(9)	121·0 (3)	121·0 (3)
C(8*a*)—C(9)—C(1*a*)	115·9 (3)	116·5 (3)
C(9)—C(1*a*)—C(4*a*)	119·4 (3)	119·2 (3)
C(1*a*)—C(4*a*)—O(10)	122·4 (3)	121·8 (3)
C(4*a*)—O(10)—C(5*a*)	119·7 (3)	119·9 (3)
O(10)—C(5*a*)—C(8*a*)	121·5 (3)	121·5 (3)
C(8*a*)—C(9)—O(1)	120·6 (3)	121·2 (3)
O(1)—C(9)—C(1*a*)	123·5 (3)	122·3 (3)
C(9)—C(1*a*)—C(1)	123·0 (3)	123·2 (3)
O(10)—C(4*a*)—C(4)	114·4 (3)	114·9 (3)
C(1*a*)—C(1)—C(2)	119·0 (4)	118·8 (3)
C(1)—C(2)—C(3)	120·3 (4)	120·9 (4)
C(2)—C(3)—C(4)	122·1 (4)	122·3 (4)
C(3)—C(4)—C(4*a*)	117·7 (4)	117·2 (4)
C(4)—C(4*a*)—C(1*a*)	123.3 (4)	123·2 (4)
C(4*a*)—C(1*a*)—C(1)	117·5 (3)	117·6 (3)
C(1*a*)—C(1)—N	118·3 (3)	118·6 (3)
C(2)—C(1)—N	122·6 (4)	122·6 (4)
C(1)—N—C(11)	126·9 (3)	122·5 (3)
N—C(11)—C(12)	118·5 (4)	119·7 (4)
N—C(11)—C(16)	123·3 (4)	120·9 (4)
C(11)—C(12)—C(13)	120·7 (4)	120·3 (4)
C(12)—C(13)—C(14)	120·6 (4)	120·6 (4)
C(13)—C(14)—C(15)	119·2 (4)	119·3 (4)
C(14)—C(15)—C(16)	120·0 (4)	119·6 (4)
C(15)—C(16)—C(11)	121·3 (4)	120·8 (4)
C(16)—C(11)—C(12)	118·1 (4)	119·4 (4)
C(13)—C(14)—O(2)	114·9 (4)	116·1 (4)
C(15)—C(14)—O(2)	125·9 (5)	124·6 (4)
C(14)—O(2)—C(17)	118·2 (4)	119·2 (4)
N···O(1)	2·648 (4)	2·626 (4)
O(1)···H	1·88 (4)	1·75 (5)
N—H	0·96 (4)	1·15 (5)
N—H···O(1)	135 (3)	142 (3)
C(1)—N—C(11)—C(16)	−46·1 (6)	−82·6 (5)
C(17)—O(2)—C(14)—C(15)	2·5 (7)	6·7 (6)
C(18)—O(3)—C(6)—C(7)	175·4 (3)	178·5 (3)
O(1)—C(9)—C(8*a*)—C(5*a*)	175·6 (4)	177·2 (4)
C(5*a*)—C(5)—C(6)—C(7)	−0·7 (6)	0·4 (6)
C(5)—C(6)—C(7)—C(8)	2·0 (6)	0·1 (6)

Table 2 (*cont.*)

	Molecule *A*	Molecule *B*
C(6)—C(7)—C(8)—C(8*a*)	−1·5 (6)	0·0 (6)
C(7)—C(8)—C(8*a*)—C(5*a*)	−0·3 (6)	−0·8 (6)
C(8)—C(8*a*)—C(5*a*)—C(5)	1·7 (6)	1·4 (6)
C(8*a*)—C(5*a*)—C(5)—C(6)	−1·2 (6)	−1·3 (6)
C(1*a*)—C(4*a*)—O(10)—C(5*a*)	−2·9 (6)	−1·3 (5)
C(4*a*)—O(10)—C(5*a*)—C(8*a*)	0·2 (6)	0·1 (5)
O(10)—C(5*a*)—C(8*a*)—C(9)	3·5 (6)	1·6 (6)
C(5*a*)—C(8*a*)—C(9)—C(1*a*)	−4·2 (6)	−2·2 (6)
C(8*a*)—C(9)—C(1*a*)—C(4*a*)	1·6 (5)	1·1 (5)
C(9)—C(1*a*)—C(4*a*)—O(10)	1·9 (6)	0·6 (6)
C(1)—C(2)—C(3)—C(4)	1·1 (6)	0·7 (7)
C(2)—C(3)—C(4)—C(4*a*)	0·7 (6)	−0·2 (6)
C(3)—C(4)—C(4*a*)—C(1*a*)	−2·2 (6)	−0·3 (6)
C(4)—C(4*a*)—C(1*a*)—C(1)	1·9 (6)	0·1 (6)
C(4*a*)—C(1*a*)—C(1)—C(2)	−0·1 (6)	0·4 (6)
C(1*a*)—C(1)—C(2)—C(3)	−1·4 (6)	−0·9 (6)

Norrestam & Palm, 1976) and thiomelin diacetate [1·367 (4) Å] (Elix, Gaul, Sterns & Samsudin, 1987). In both molecules the pyran ring deviates from planarity assuming a distorted boat conformation [$\Delta C_s(8a)$ = 1·1 (6)° in molecule *A* and $\Delta C_s(8a)$ = 0·8 (6)° in molecule *B*]. The pyran ring has been reported to take the boat conformation in hexachloroxanthene (Soderholm, Sonnerstam, Norrestam & Palm, 1976).

4-Methoxy-N-substituted aniline. The phenyl ring C(11)—C(12)—C(13)—C(14)—C(15)—C(16) is rotated from the plane of the benzene ring C(1)—C(2)—C(3)—C(4)—C(4*a*)—C(1*a*) about N—C(11) by ~ −46·1 (6)° in molecule *A* and ~ −82·6 (5)° in molecule *B* to avoid short non-bonded interactions between H(2) and C(16) (2·642 Å) in molecule *A* and between H(2) and C(11) (2·508 Å) in molecule *B*. The bond distances of N—C(1) [1·371 (5) Å in molecule *A* and 1·361 (5) Å in molecule *B*] and N—C(11) [1·422 (5) Å in molecule *A* and 1·430 (5) Å in molecule *B*] agree with values reported for the corresponding bond distances [1·370 (4) and 1·408 (4) Å respectively] in 1-amino-4-phenylamino-9,10-anthracenedione (Kurucsev, Snow & Tiekink, 1987).

An intramolecular N—H···O bond (N···O = 2·648 and 2·626 Å in molecules *A* and *B* respectively) exists between the carbonyl O atoms substituting in the pyranoid ring and the N atom in the 4-methoxyaniline group (Table 2).

Terminal methoxy group. Each of the methoxy groups lies nearly in the plane of the respective ring at which it substitutes, as revealed by the torsion angles C(17)—O(2)—C(14)—C(15) [2·5 (7)° in molecule *A* and 6·7 (6)° in molecule *B*] and C(18)—O(3)—C(6)—C(7) [175·4 (3)° in molecule *A* and 178·5 (3)° in molecule *B*].

The intermolecular contacts are van der Waals, the closest contacts* being between C(6) and $C(4a')^{\mathrm{i}}$ (3·397 Å) and between C(3′) and $O(2')^{\mathrm{ii}}$ (3·268 Å).

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* Prime for atoms in molecule *B*. Symmetry code: (i) *x*, *y*, *z*; (ii) $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$.

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References

Chu, S. S. C. & Yang, H. T. (1977). *Acta Cryst.* B33, 2291–2293.

Elix, J. A., Gaul, K. L., Sterns, M. & Samsudin, Mohd. Wahid bin (1987). *Aust. J. Chem.* **40**, 1169–1178.

Kurucsev, T., Snow, M. R. & Tiekink, E. R. T. (1987). *Acta Cryst.* C43, 2226–2228.

Lassen, N., Bogeso, K. P., Hansen, P. B., Buss, J. L. M. & Bigler, A. J. (1980). *Chem. Abstr.* **93**, 8028f.

Pfister, J. R. (1980). *Chem. Abstr.* **93**, 239232j.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

Soderholm, M., Sonnerstam, U., Norrestam, R. & Palm, T. B. (1976). *Acta Cryst.* B32, 3013–3018.

Vinod, G. & Gupta, S. R. (1979). *Bull. Chem. Soc. Jpn*, **52**(12), 3679–3681.

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1:2 Complexes of (Thio)Morpholinium Derivatives and the Electron Acceptor 7,7,8,8-Tetracyano-*p*-quinodimethane. Part I. *N*-Methyl-*N*-ethylthiomorpholinium Di-7,7,8,8-tetracyano-*p*-quinodimethanide METM(TCNQ)$_2$ and *N*-Methyl-*N*-butylthiomorpholinium Di-7,7,8,8-tetracyano-*p*-quinodimethanide MBTM(TCNQ)$_2$*

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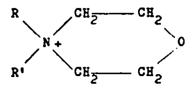
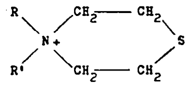
Abstract. METM(TCNQ)$_2$, $C_7H_{16}NS^{+}.2C_{12}H_4N_4^{1/2-}$, $M_r = 554{\cdot}7$, triclinic, $P\bar{1}$, $a = 15{\cdot}509\,(5)$, $b = 15{\cdot}023\,(6)$, $c = 6{\cdot}513\,(2)$ Å, $\alpha = 90{\cdot}70\,(3)$, $\beta = 101{\cdot}95\,(2)$, $\gamma = 107{\cdot}44\,(2)°$, $V = 1412\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}304$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}156$ mm^{-1}, $F(000) = 578$, $T = 294$ K, $R = 0{\cdot}058$ for 6536 observed reflections. Transformation to conventional cell by (0,0,−1/0,−1,0/−1,0,0). MBTM(TCNQ)$_2$, $C_9H_{20}NS^{+}.2C_{12}H_4N_4{}^{1/2-}$, $M_r = 582{\cdot}7$, triclinic, $P\bar{1}$, $a = 15{\cdot}685\,(2)$, $b = 15{\cdot}573\,(2)$, $c = 6{\cdot}561\,(1)$ Å, $\alpha = 94{\cdot}63\,(1)$, $\beta = 103{\cdot}10\,(1)$, $\gamma = 100{\cdot}62\,(1)°$, $V = 1522\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}272$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}149$ mm^{-1}, $F(000) = 610$, $T = 294$ K, $R = 0{\cdot}123$ for 4816 observed reflections. Transformation to conventional cell by (0,0,−1/−1,0,−1/0,1,0). The packing in the two compounds is very similar: zigzag stacks are connected to form sheets parallel to the *bc* plane. There are two independent molecules *A* and *B* per stack; all overlaps are large and of type I. METM(TCNQ)$_2$ has the shorter N$^+\cdots$TCNQ distance and a significant charge difference $\rho^s_A - \rho^s_B = -0{\cdot}34\,(4)$ e. The charge difference for MBTM(TCNQ)$_2$, $\rho^s_A - \rho^s_B = 0{\cdot}29\,(19)$ e, has opposite sign.

Introduction. In the course of a systematic study of the charge transfer complexes of substituted (<u>T</u>hio)morpholinium groups $RR'(\underline{\mathrm{T}})\mathrm{M}^+$ [(I) R, R' = —H or —alkyl] with the organic acceptor 7,7,8,8-tetracyanoquinodimethane [TCNQ, (II)], a substantial number (*ca* 40) of new members of this class have been prepared. For a selected series of 1:2 complexes, the crystal structures have been determined to find qualitative relationships between packing characteristics and physical properties.



RR'M



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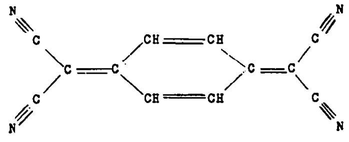

TCNQ

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* 1:2 *N*-Ethyl-*N*-methylthiomorpholinium and *N*-Butyl-*N*-methylthiomorpholinium salts with the radical anion of 2,2′-(2,5-cyclohexadiene-1,4-diylidene)bispropanedinitrile.

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