Acta Cryst. (1994). C**50**, 1139–1141

1:2 Complexes of (Thio)Morpholinium Derivatives and the Electron Acceptor 7,7,8,8-Tetracyano-*p*-quinodimethane. VII.† Triclinic form of *N*,*N*-Dimethylmorpholinium Di-7,7,8,8-tetracyano-*p*-quinodimethanide, DMM(TCNQ)$_2$ (II), at 294 K

Rudy J. J. Visser, Jan L. de Boer* and Aafje Vos

Materials Science Centre, Department of Inorganic Chemistry, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(*Received* 17 *March* 1993; *accepted* 13 *October* 1993)

Abstract

The title compound DMM(TCNQ)$_2$ (II), $C_6H_{14}NO^+.2C_{12}H_4N_4^{1/2-}$, is the triclinic form of the 1:2 *N*,*N*-dimethylmorpholinium salt with the radical anion of 2,2′-(2,5-cyclohexadiene-1,4-diylidene)bispropanedinitrile. At room temperature the segregated TCNQ stacks in the compound are almost uniform with reasonably large overlaps of distorted type I. Parallel stacks are connected to form sheets by electrostatically favourable N···H contacts of ~2.7 Å. The sheets are corrugated with successive sheets having direct intermolecular contacts. The cations, which are dynamically disordered over two chair conformations, are packed in channels along the stacks. There is a strong charge difference $\rho^s_B - \rho^s_A = 0.72\,(8)$ e between the inequivalent TCNQ groups *A* and *B* alternating in the stacks.

Comment

The present paper is part of a series of structure determinations of 1:2 salts [*RR*′(T)M](TCNQ)$_2$ of *N*-substituted (thio)morpholinium *RR*′(T)M$^+$ (*R*,*R*′ = H or alkyl) and TCNQ. A general introduction to the series including definitions of different quantities is given in Part I (Visser, Bouwmeester, de Boer & Vos, 1990). Monoclinic (I) and triclinic (II) crystals of DMM(TCNQ)$_2$ are grown by slowly cooling hot solutions of DMM iodide and neutral TCNQ in acetonitrile. For references to (I) (294 K) and to low-temperature phases of (I) and (II), see Steurer, Visser, van Smaalen & de Boer (1987).

Two independent TCNQ molecules, *A* and *B*, alternate in the zigzag stacks. Both molecules are approximately perpendicular to the stacking axis *c*, with inclinations of 4.7 and 5.4°, respectively. The corrugated sheet structure of DMM(TCNQ)$_2$ (II) is exceptional for the class of [*RR*′(T)M](TCNQ)$_2$ salts. All other compounds of this class contain 'flat' sheets which are not in direct contact with each other, but separated by a layer of cations (*e.g.* Part I, Fig. 4). Also for other classes of TCNQ compounds the corrugated sheet structure is rare. To our knowledge, it has only been observed in acridinium(TCNQ)$_2$ (Kobayashi, 1974) and quinolinium(TCNQ)$_2$ (Kobayashi, Marumo & Saito, 1971). The charge localization in DMM(TCNQ)$_2$ (II), which is outstandingly large for the class of [*RR*′(T)M](TCNQ)$_2$ compounds, has a strong impact on its physical properties. At room temperature its electrical conductivity is, for example, at least three orders of magnitude smaller than in other [*RR*′(T)M](TCNQ)$_2$ salts with almost uniform stacks (Visser, van Heemstra & de Boer, 1982).

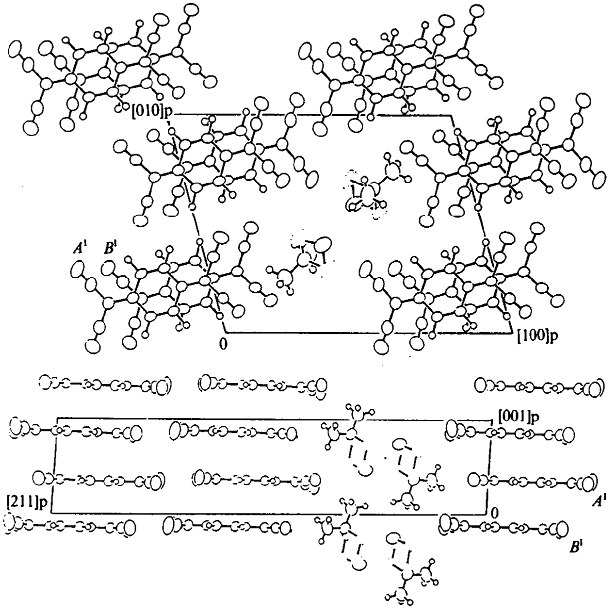


Fig. 1. Projections of the DMM(TCNQ)$_2$ (II) structure: above, along [001]; below, along the molecular axis **M** (defined in Table 1 of Part I) of one layer of cations and anions. Each dashed C atom of DMM represents two fractional atoms. [Symmetry code: (I) −*x*, −*y*, −*z*.]

Experimental

Crystal data

$C_6H_{14}NO^+.2C_{12}H_4N_4^{1/2-}$
M_r = 524.6
Triclinic
$P\bar{1}$
a = 16.487 (3) Å
b = 12.909 (3) Å
c = 6.783 (1) Å
α = 103.24 (2)°
β = 99.60 (2)°
γ = 102.95 (2)°

D_x = 1.307 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 22 reflections
θ = 16.9–19.9°
μ = 0.079 mm^{-1}
T = 294 K
Twinned needles
0.25 × 0.25 × 0.10 mm

---

† Part VI: Visser, de Boer & Vos (1990).

V = 1333 (1) Å^3
Z = 2

Dark violet

Data collection

Enraf-Nonius CAD-4F diffractometer
ω-2θ scans
Absorption correction: none
7773 measured reflections
7773 independent reflections
6124 observed reflections [$I \geq 0$]

$\theta_{\max}$ = 30°
h = −22 → 21
k = −18 → 17
l = 0 → 9
3 standard reflections
frequency: 150 min
intensity variation: ±2.4%

Refinement

Refinement on F
R = 0.099
wR = 0.075
S = 1.62
4485 [$F > 2\sigma(F)$] reflections
424 parameters
Only H-atom U's refined
$(\Delta/\sigma)_{\max}$ = 0.024
$\Delta\rho_{\max}$ = 0.30 e Å^{-3}
$\Delta\rho_{\min}$ = −0.29 e Å^{-3}

Extinction correction: type I (Becker & Coppens, 1974)
Extinction coefficient: up to 15% in $|F|$
Atomic scattering factors from Cromer & Mann (1968) for non-H, and Stewart, Davidson & Simpson (1965) for H atoms

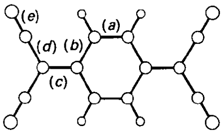
Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
N1	−0.0751 (2)	−0.4367 (2)	−0.6382 (5)	0.078 (1)
C2	−0.0302 (2)	−0.3492 (2)	−0.5728 (4)	0.050 (1)
C3	0.0229 (2)	−0.2383 (2)	−0.4923 (4)	0.041 (1)
C4	−0.0241 (2)	−0.1575 (2)	−0.4582 (4)	0.045 (1)
N5	−0.0649 (2)	−0.0971 (2)	−0.4331 (4)	0.066 (1)
C6	0.1109 (2)	−0.2115 (2)	−0.4506 (4)	0.039 (1)
C7	0.1619 (2)	−0.0989 (2)	−0.3711 (4)	0.042 (1)
C8	0.2478 (2)	−0.0739 (2)	−0.3318 (4)	0.045 (1)
C9	0.2911 (2)	−0.1592 (2)	−0.3696 (4)	0.044 (1)
C10	0.2396 (2)	−0.2719 (2)	−0.4485 (4)	0.046 (1)
C11	0.1537 (2)	−0.2974 (2)	−0.4871 (4)	0.043 (1)
N12	0.4506 (2)	−0.2931 (3)	−0.4005 (5)	0.090 (2)
C13	0.4205 (2)	−0.2219 (3)	−0.3697 (5)	0.062 (1)
C14	0.3790 (2)	−0.1350 (2)	−0.3338 (4)	0.051 (1)
C15	0.4325 (2)	−0.0241 (3)	−0.2589 (5)	0.068 (2)
N16	0.4735 (2)	0.0655 (3)	−0.2005 (6)	0.104 (2)
N17	−0.1907 (2)	−0.4832 (2)	−0.2329 (5)	0.092 (1)
C18	−0.1485 (2)	−0.3948 (2)	−0.1541 (5)	0.058 (1)
C19	−0.0996 (2)	−0.2837 (2)	−0.0590 (4)	0.045 (1)
C20	−0.1475 (2)	−0.2070 (2)	−0.0117 (4)	0.047 (1)
N21	−0.1880 (2)	−0.1473 (2)	0.0274 (4)	0.068 (1)
C22	−0.0091 (2)	−0.2523 (2)	−0.0142 (4)	0.041 (1)
C23	0.0380 (2)	−0.1395 (2)	0.0674 (4)	0.043 (1)
C24	0.1251 (2)	−0.1084 (2)	0.1102 (4)	0.045 (1)
C25	0.1722 (2)	−0.1878 (2)	0.0759 (4)	0.042 (1)
C26	0.1247 (2)	−0.3009 (2)	−0.0056 (4)	0.045 (1)
C27	0.0378 (2)	−0.3316 (2)	−0.0491 (4)	0.044 (1)
N28	0.3469 (2)	−0.2982 (2)	0.0525 (5)	0.086 (2)
C29	0.3099 (2)	−0.2340 (2)	0.0836 (5)	0.057 (1)
C30	0.2623 (2)	−0.1555 (2)	0.1206 (4)	0.047 (1)
C31	0.3088 (2)	−0.0429 (3)	0.2045 (5)	0.055 (1)
N32	0.3455 (2)	0.0485 (2)	0.2732 (5)	0.084 (1)
N33	0.3450 (2)	0.3389 (2)	−0.3683 (4)	0.066 (1)
C34*a*	0.3549 (5)	0.4484 (8)	−0.2309 (16)	0.048 (3)
C34*b*	0.3188 (7)	0.4248 (11)	−0.195 (3)	0.108 (7)
C35*a*	0.3431 (7)	0.4291 (8)	−0.015 (2)	0.057 (4)
C35*b*	0.3788 (9)	0.4690 (10)	−0.017 (3)	0.114 (8)
O36	0.4241 (2)	0.4043 (2)	0.0673 (3)	0.081 (1)
C37*a*	0.4077 (6)	0.2907 (9)	−0.0665 (18)	0.056 (4)
C37*b*	0.4475 (9)	0.3205 (13)	−0.066 (2)	0.158 (8)
C38*a*	0.4228 (11)	0.2909 (13)	−0.270 (2)	0.078 (6)
C38*b*	0.4025 (13)	0.2923 (14)	−0.275 (2)	0.097 (7)
C39	0.3701 (2)	0.3674 (4)	−0.5529 (8)	0.104 (3)
C40	0.2602 (2)	0.2542 (3)	−0.4408 (6)	0.090 (2)

Table 2. *Bond lengths* (Å) *in the* TCNQ *molecule*

Bonds in the same group are equivalent for the adopted *mmm* TCNQ symmetry.



	TCNQ *A*		TCNQ *B*	
(*a*)	C7—C8	1.346 (4)	C23—C24	1.362 (4)
	C10—C11	1.346 (4)	C26—C27	1.359 (4)
(*b*)	C6—C7	1.433 (3)	C22—C23	1.418 (3)
	C6—C11	1.440 (4)	C22—C27	1.417 (4)
	C8—C9	1.439 (4)	C24—C25	1.419 (4)
	C9—C10	1.436 (3)	C25—C26	1.423 (3)
(*c*)	C3—C6	1.377 (4)	C19—C22	1.415 (4)
	C9—C14	1.379 (4)	C25—C30	1.409 (4)
(*d*)	C2—C3	1.427 (3)	C18—C19	1.417 (3)
	C3—C4	1.433 (4)	C19—C20	1.413 (4)
	C13—C14	1.435 (5)	C29—C30	1.419 (5)
	C14—C15	1.428 (4)	C30—C31	1.414 (4)
(*e*)	C2—N1	1.143 (4)	C18—N17	1.145 (4)
	C4—N5	1.141 (4)	C20—N21	1.143 (4)
	C13—N12	1.134 (5)	C29—N28	1.137 (5)
	C15—N16	1.140 (4)	C31—N32	1.144 (4)

Table 3. *Crystal structure data block*

For definitions see Part I of the series (Visser, Bouwmeester, de Boer & Vos, 1990). E.s.d.'s of averages *a* to *e* (Table 2) are taken as 0.004 Å.

TCNQ *A*			
G	0.20089 (16)	−0.18578 (21)	−0.41058 (40)
L	0.063823	0.018506	0.028480
M	0.003428	0.080464	0.047257
N	0.002118	−0.005224	0.145512
U	0.0437 (11)		
TCNQ *B*			
G	0.08143 (17)	−0.21996 (20)	0.03077 (39)
L	0.063926	0.022687	0.031755
M	0.000089	0.079288	0.047891
N	0.001754	−0.006557	0.144624
U	0.0439 (11)		

Charge

	ρ (e)	*a*	*b*	*c*	*d*	*e*
TCNQ *A*	0.15 (6)	1.346	1.437	1.378	1.431	1.140
TCNQ *B*	0.92 (6)	1.361	1.419	1.412	1.416	1.142

Stack

B—*A*	t^c = 0.115 eV	ν = 1.964**L**−0.329**M**−3.345**N**
A—*B*$^{\rm i}$	t^c = 0.087 eV	ν = −1.760**L**−0.220**M**−3.412**N**

Symmetry code: (i) $x, y, z-1$.

The diffractometer was equipped with a graphite monochromator and beam flattener (Helmholdt & Vos, 1977). Least-squares block-matrix refinement was carried out with one independent molecule per block. The observed DMM disorder over two chair conformations was checked so as to verify that it was not caused by incorrect choice of centrosymmetric space group. For the O, N and C(methyl) atoms of DMM, the disorder was accounted for by increase of thermal tensor *U*, and for each of the DMM ring C atoms by use of two fractional atoms, each with occupancy 0.5. Computations were carried out on a Cyber 170/760 with the *XRAY* (1976) system and local crystallographic programs.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71739 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1060]

References

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 148–153.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
Helmholdt, R. B. & Vos, A. (1977). *Acta Cryst.* **A33**, 456–465.
Kobayashi, H. (1974). *Bull. Chem. Soc. Jpn*, **47**, 1346–1352.
Kobayashi, H., Marumo, F. & Saito, Y. (1971). *Acta Cryst.* **B27**, 373–378.
Steurer, W., Visser, R. J. J., van Smaalen, S. & de Boer, J. L. (1987). *Acta Cryst.* **B43**, 567–574.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Visser, R. J. J., Bouwmeester, H. J. M., de Boer, J. L. & Vos, A. (1990). *Acta Cryst.* **C46**, 852–856.
Visser, R. J. J., de Boer, J. L. & Vos, A. (1990). *Acta Cryst.* **C46**, 869–871.
Visser, R. J. J., van Heemstra, T. W. L. & de Boer, J. L. (1982). *Mol. Cryst. Liq. Cryst.* **85**, 265–269.
XRAY (1976). Dutch version of *The XRAY System of Crystallographic Programs.* Technical Report TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Acta Cryst. (1994). **C50**, 1141–1143

Indan-2,2-dicarboxylic Acid, $C_{11}H_{10}O_4$

J. Gabriel Garcia* and Joel D. Enas

Lawrence Berkeley Laboratory, UC-Berkeley, Berkeley, CA 94720, USA

Frank R. Fronczek

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804, USA

(*Received* 22 *April* 1993; *accepted* 29 *October* 1993)

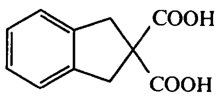
Abstract

The cyclopentene ring has an envelope conformation with the C atom carrying the carboxyl group lying 0.355 (2) Å out of the best plane of the other four C atoms. The cyclopentene torsion angle along the fusion of both rings has a magnitude of −2.5 (3)°. The carboxyl groups adopt synperiplanar conformations with C—C—C—O torsion angles of 4.5 (3) and −20.3 (3)°. The C=C distance at the ring fusion is 1.379 (3) Å. The C=O distances are 1.207 (3) and 1.215 (3) Å.

Comment

As part of an ongoing structural study of the intermediates in the synthesis of atipamezole (Garcia & Enas, 1993), indan-2,2-dicarboxylic acid was required. The title compound was prepared by condensing *α*,*α*′-dibromo-*o*-xylene with diethyl malonate and sodium ethoxide followed by basic hydrolysis (Carlson, Quina, Zarnegar & Whitten, 1975).

The carboxyl groups adopt synperiplanar conformations (Klyne & Prelog, 1960) with torsion angles O1—C10—C2—C3 of 4.5 (3)° and O3—C11—C2—C1 of −20.3 (3)°. Structural data for cyclobutane-1,1-dicarboxylic acid (Santarsiero, 1990), cyclopropane-1,1-dicarboxylic acid (Meester, Schenk & MacGillavry, 1971), 2,2-dimethyl-4,5-dinitroindan (Garcia, Enas & Fronczek, 1993*a*), 2-ethyl-2-nitroindan-1,3-dione (Garcia, Enas, Chang & Fronzek, 1993) and 2-acylindan-1-one (Garcia, Enas & Fronczek, 1993*b*) are in agreement with those of the title compound, (I).



(I)

The cyclopentene ring adopts an envelope conformation [torsion angles ω_1 (C1—C8—C9—C3), ω_2 (C8—C9—C3—C2), ω_3 (C9—C3—C2—C1), ω_4 (C3—C2—C1—C8) and ω_5 (C2—C1—C8—C9) of −2.5 (3), −11.7 (3), 20.5 (2), −21.9 (2) and 15.6 (3)°, respectively] that is slightly distorted from the ideal envelope conformation of cyclopentene [torsion angles $\omega_1 = 0$, $\omega_2 = -15$, $\omega_3 = 24$, $\omega_4 = -24$ and $\omega_5 = 15°$ (Bartlett, Kimura, Nakayama & Watson, 1979)].

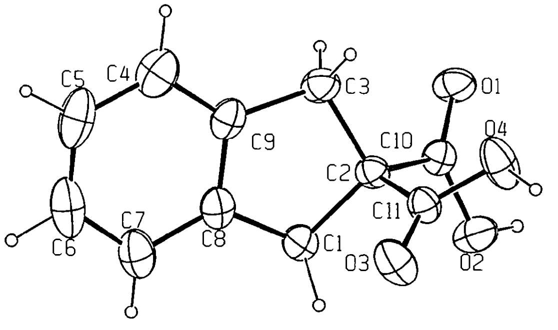


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the title molecule representing heavy atoms as 40% probability ellipsoids and H atoms as circles of arbitrary radii.

Acta Crystallographica Section C
ISSN 0108-2701 ©1994