Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Rao, S. T., Westhof, E. & Sundaralingam, M. (1981). *Acta Cryst.* A**37**, 421-425.
Rogers, D. (1981). *Acta Cryst.* A**37**, 734-741.
Spek, A. L. (1991). *PLATON*. Univ. of Utrecht, The Netherlands.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063-5070

Acta Cryst. (1993). C**49**, 1837–1840

Structure Determinations of (*dl*)-*trans*-3-Hydroxy-5-iodomethyl-2,2-diphenyltetrahydrofuran and (*dl*)-*trans*-*N*,*N*,*N*-Trimethyl-(3-hydroxy-2,2-diphenyltetrahydro-5-furyl)methylammonium Iodide

KARLA FRYDENVANG

Department of Organic Chemistry, Royal Danish School of Pharmacy, Universitetsparken 2, DK-2100 Copenhagen, Denmark

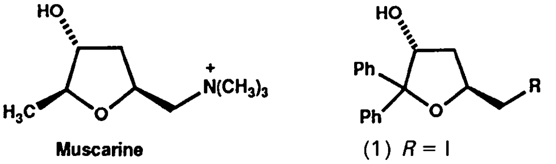
(*Received* 3 *December* 1992; *accepted* 19 *April* 1993)

Abstract

The conformation of the five-membered ring in muscarine-related compounds was studied. The conformations observed in the two title compounds, (1) 5-iodomethyl-2,2-diphenyltetrahydrofuran-3-ol and (2) trimethyl[(3-hydroxy-2,2-diphenyltetrahydro-5-furyl)methyl]ammonium iodide, are slightly different. In the iodomethyl compound the ring adopts an E_3 envelope conformation in which the C atom connected to the hydroxy group is out of the best plane through the remaining ring atoms. The ring adopts a $^4T_3$ twist conformation in the iodide salt with the C atom connected to the hydroxy group and the methylene C atom out of the plane of the ring. In both cases, the hydroxy group is in an axial orientation. The puckering amplitudes are of the same magnitude (40.8 and 41.5°, respectively). The crystal packing in the iodomethyl compound is stabilized by van der Waals contacts and that of the iodide salt by van der Waals contacts and electrostatic interactions. In the latter, a hydrogen bond is also observed between the hydroxy group and the iodide ion.

Comment

The structure determinations of the two title compounds were performed in order to study the conformations of the five-membered rings and to obtain information about the relative orientations, *cis* or *trans*, of the ring substituents. A series of cholinergic compounds has been analyzed in order to obtain information about the dependence of the flexibility of the five-membered ring on the substituents (Jellinek, 1957; Frydenvang & Jensen, 1990, 1993). A five-membered ring is present in many cholinergic compounds, agonists as well as antagonists. Muscarine is an agonist in parts of the cholinergic nervous system whereas compound (2) is expected to be an antagonist on the basis of earlier studies of oxathiolane compounds (Angeli *et al.*, 1986).



Muscarine

(1) *R* = I
(2) *R* = $^+N(CH_3)_3$

The final results of the structure determinations are given in Table 1 and 2, and the compounds are shown in Fig. 1. The substituents on the five-membered ring

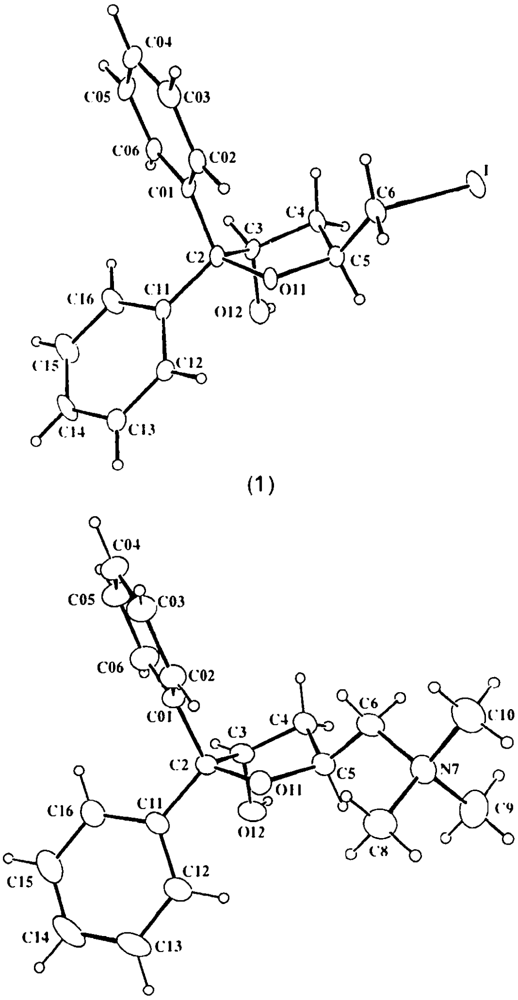
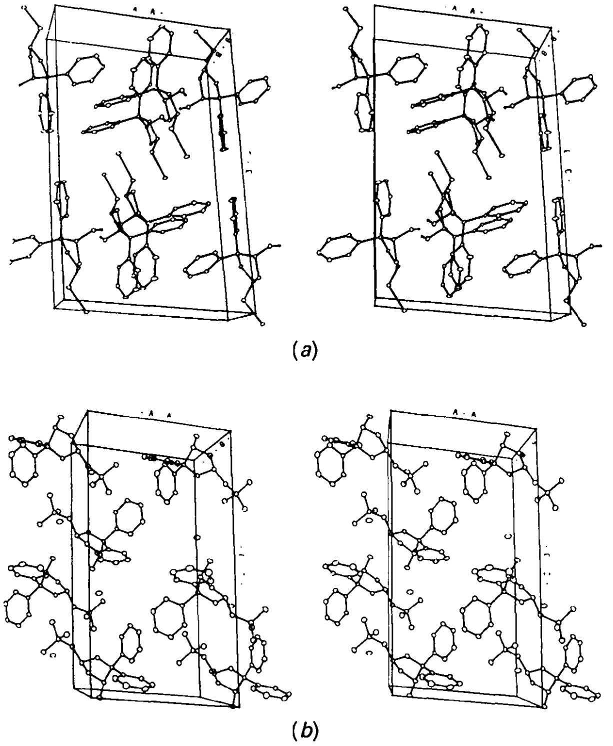


Fig. 1. The title compounds shown with displacement ellipsoids and atomic labelling (*ORTEP*; Johnson, 1976).

are *trans* in both cases. The conformations of the five-membered rings are slightly different in the two compounds (E_3 and $^4T_3$ for compounds (1) and (2), respectively) but the puckering amplitudes are nearly the same. The conformations and amplitudes are compared with the results of previous studies of the muscarine ion in Table 3. It is found that the two phenyl groups connected to C2 have no influence on the preferred conformation of the ring. The iodomethyl group of (1) is observed in an *anti* orientation [O—C—C—I 175.3 (3)°], while the quaternary ammonium group in (2) is observed in a *gauche* orientation [O—C—C—N 87.8 (2)°]. This orientation of the ammonium group is energetically the most favourable and has been found in all published structures containing the muscarine ion (Jellinek, 1957; Frydenvang & Jensen, 1990, 1993). However, theoretical calculations (Frydenvang, 1989) show that the *anti* orientation can be obtained without excessive energy consumption. The *anti* orientation of the quaternary ammonium group can therefore still be the biologically active conformation at the receptor site.

The crystal packing of (1) is stabilized by van der Waals interactions (Fig. 2). Contacts are observed between the iodide ion and one of the aromatic rings [I···C04 $(2-x, 1-y, 2-z)$ 3.640 (5) Å]. The crystal packing of (2) (Fig. 2) is stabilized by electrostatic interactions and van der Waals contacts. A hydrogen bond is observed between the hydroxy group and the iodide ion (Table 2), and several close contacts are observed between the iodide ions and the quaternary ammonium group. The positive charge is delocalized on the C atoms connected to the N atom and contacts are observed to the iodide ion [I···C6 $(2-x, \frac{1}{2}+y, \frac{1}{2}-z)$ 3.793 (2) Å]. Preferred contacts from the quaternary ammonium group to an aromatic ring system, as described by Dhanens, Lacombe, Lehn & Vigneron (1984), are not observed in (2).


(*a*)

(*b*)

Fig. 2. Stereo drawings of the crystal packing in (*a*) compound (1) and (*b*) compound (2); *x* is horizontal, *z* vertical and *y* into the plane of the paper.

Experimental

Compound (1)

Crystal data

$C_{17}H_{17}O_2I$
$M_r = 380.23$
Monoclinic
$P2_1/n$
$a = 12.764$ (2) Å
$b = 5.768$ (2) Å
$c = 20.129$ (5) Å
$\beta = 96.18$ (2)°
$V = 1473$ (1) Å^3
$Z = 4$
$D_x = 1.714$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 22 reflections
$\theta = 37.97$-$46.77°$
$\mu = 17.24$ mm^{-1}
$T = 122$ K
Needle
0.36 × 0.15 × 0.05 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
Profile data collected by $\omega/2\theta$ scans
Absorption correction: *ABSCOR* (*SDP*; B. A. Frenz & Associates, Inc., 1982)
$T_{\min} = 0.076$, $T_{\max} = 0.485$
4275 measured reflections
3023 independent reflections

2499 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.070$
$\theta_{\max} = 75.0°$
$h = -15 \rightarrow 3$
$k = 0 \rightarrow 7$
$l = -25 \rightarrow 25$
3 standard reflections monitored every 300 reflections intensity variation: −20.3% (corrected)

Refinement

Refinement on F
Final $R = 0.047$
$wR = 0.063$
$S = 1.305$
2499 reflections
202 parameters
Calculated weights $w = 1/[\sigma^2(F)+(0.080F^2)/4]$

$(\Delta/\sigma)_{\max} = 0.30$
$\Delta\rho_{\max} = 0.319$ e Å^{-3}
$\Delta\rho_{\min} = -0.216$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (2)

Crystal data

$C_{20}H_{26}O_2N^+.I^-$
$M_r = 439.34$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$P2_1/c$
a = 10.599 (2) Å
b = 9.270 (3) Å
c = 19.641 (4) Å
β = 96.17 (1)°
V = 1919 (1) Å^3
Z = 4
D_x = 1.521 Mg m^{-3}

Cell parameters from 22 reflections
θ = 19.67–22.83°
μ = 1.660 mm^{-1}
T = 122 K
Prism
0.25 × 0.20 × 0.10 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data collected by $\omega/2\theta$ scans
Absorption correction: *ABSCOR* (*SDP*; B. A. Frenz & Associates, Inc., 1982)
$T_{\min}$ = 0.3676, $T_{\max}$ = 0.7502
16 243 measured reflections
10 405 independent reflections

6079 observed reflections [$I > 5\sigma(I)$]
$R_{\rm int}$ = 0.046
$\theta_{\max}$ = 38.00°
$h = 0 \rightarrow 18$
$k = -16 \rightarrow 16$
$l = -33 \rightarrow 33$
3 standard reflections monitored every 300 reflections
intensity variation: −4.0% (corrected)

Refinement

Refinement on F
Final R = 0.039
wR = 0.052
S = 2.323
6079 reflections
238 parameters
Calculated weights $w = 1/[\sigma^2(F)+(0.020F^2)/4]$

$(\Delta/\sigma)_{\max}$ = 0.19
$\Delta\rho_{\max}$ = 2.575 e Å^{-3}
$\Delta\rho_{\min}$ = −0.639 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
(1)				
I	0.83887 (2)	0.72774 (6)	1.01322 (1)	1.773 (6)
C01	1.0833 (3)	0.5846 (8)	0.8036 (2)	1.10 (7)
C02	1.1392 (4)	0.7584 (8)	0.8403 (3)	1.32 (8)
C03	1.2443 (4)	0.7228 (9)	0.8651 (3)	1.64 (9)
C04	1.2957 (3)	0.519 (1)	0.8528 (3)	1.74 (9)
C05	1.2405 (3)	0.346 (1)	0.8160 (3)	1.66 (8)
C06	1.1353 (3)	0.3764 (9)	0.7922 (2)	1.47 (8)
C11	0.9586 (3)	0.6861 (9)	0.7017 (2)	1.16 (7)
C12	0.9166 (3)	0.8967 (9)	0.6778 (2)	1.34 (8)
C13	0.9046 (3)	0.943 (1)	0.6097 (2)	1.59 (8)
C14	0.9343 (5)	0.783 (1)	0.5645 (3)	2.1 (1)
C15	0.9774 (5)	0.573 (1)	0.5884 (3)	2.7 (1)
C16	0.9895 (4)	0.526 (1)	0.6561 (3)	2.2 (1)
C2	0.9674 (3)	0.6258 (8)	0.7760 (2)	1.06 (7)
C3	0.8978 (3)	0.4174 (9)	0.7911 (2)	1.23 (8)
C4	0.8822 (3)	0.4618 (9)	0.8638 (2)	1.30 (8)
C5	0.8711 (4)	0.7239 (8)	0.8667 (3)	1.18 (8)
C6	0.9227 (4)	0.833 (1)	0.9306 (2)	1.55 (8)
O11	0.9237 (2)	0.8136 (6)	0.8112 (2)	1.11 (5)
O12	0.8009 (2)	0.4394 (7)	0.7489 (2)	1.83 (7)
(2)				
I	0.85197 (2)	0.90601 (2)	0.12206 (1)	2.564 (3)
C01	0.6724 (2)	0.8199 (2)	0.3494 (1)	1.50 (3)
C2	0.7633 (2)	0.9066 (2)	0.4008 (1)	1.49 (3)
C3	0.8115 (2)	0.8066 (2)	0.4612 (1)	1.76 (3)
C4	0.9160 (2)	0.7244 (2)	0.4306 (1)	1.82 (3)
C5	0.9770 (2)	0.8433 (2)	0.3922 (1)	1.74 (3)
C6	1.0379 (2)	0.7864 (2)	0.3319 (1)	1.93 (3)
N7	1.1467 (2)	0.8757 (2)	0.3087 (1)	2.00 (3)
C8	1.1016 (2)	1.0242 (3)	0.2896 (2)	2.48 (4)
C9	1.2559 (2)	0.8806 (4)	0.3634 (2)	3.12 (5)
C10	1.1866 (2)	0.8014 (4)	0.2466 (2)	2.95 (5)
C02	0.6784 (2)	0.8391 (3)	0.2799 (1)	1.77 (3)
C03	0.5989 (2)	0.7601 (3)	0.2320 (1)	2.25 (4)
C04	0.5147 (2)	0.6597 (3)	0.2531 (1)	2.45 (4)
C05	0.5064 (2)	0.6405 (3)	0.3218 (2)	2.66 (4)
C06	0.5841 (2)	0.7219 (3)	0.3705 (1)	2.31 (4)
C11	0.7061 (2)	1.0487 (2)	0.4215 (1)	1.70 (3)
C16	0.5775 (2)	1.0607 (3)	0.4295 (1)	2.14 (4)
C15	0.5267 (2)	1.1916 (3)	0.4485 (2)	2.78 (5)
C14	0.6038 (3)	1.3105 (3)	0.4610 (2)	3.07 (5)
C13	0.7336 (3)	1.2998 (3)	0.4548 (2)	3.13 (5)
C12	0.7832 (2)	1.1694 (3)	0.4351 (2)	2.54 (4)
O11	0.8767 (1)	0.9414 (2)	0.36878 (9)	1.64 (2)
O12	0.8599 (2)	0.8900 (2)	0.51895 (9)	2.11 (3)

Table 2. *Bond lengths* (Å), *bond angles* (°), *selected torsion angles* (°) *and hydrogen-bond dimensions* (Å, °)

	(1)	(2)
C2—O11	1.440 (6)	1.451 (3)
C2—C11	1.528 (6)	1.524 (3)
C2—C01	1.542 (5)	1.543 (3)
C2—C3	1.544 (6)	1.548 (3)
C3—C4	1.520 (7)	1.521 (3)
C3—O12	1.428 (5)	1.422 (3)
C4—C5	1.520 (7)	1.519 (3)
C5—O11	1.460 (6)	1.437 (3)
C5—C6	1.517 (7)	1.502 (3)
C6—I	2.159 (5)	
C6—N7		1.529 (3)
N7—C8		1.492 (3)
N7—C9		1.493 (3)
N7—C10		1.501 (4)
C01—C02		1.385 (3)
C02—C03	1.396 (7)	1.401 (3)
C03—C04	1.380 (8)	1.384 (4)
C04—C05	1.390 (7)	1.373 (4)
C05—C06	1.388 (6)	1.411 (4)
C01—C06	1.402 (7)	1.398 (3)
C11—C12	1.393 (7)	1.394 (3)
C12—C13	1.390 (7)	1.389 (4)
C13—C14	1.378 (8)	1.398 (4)
C14—C15	1.395 (9)	1.378 (4)
C15—C16	1.382 (8)	1.394 (4)
C11—C16	1.390 (8)	1.393 (3)
C02—C01—C06	118.6 (4)	118.6 (2)
C01—C02—C03	120.0 (4)	120.5 (2)
C02—C03—C04	121.2 (5)	120.7 (2)
C03—C04—C05	119.0 (4)	119.6 (2)
C04—C05—C06	120.5 (5)	120.1 (2)
C01—C06—C05	120.6 (4)	120.5 (2)
C02—C01—C2	119.7 (4)	119.0 (2)
C06—C01—C2	121.7 (4)	122.4 (2)
C12—C11—C16	118.5 (4)	118.4 (2)
C11—C12—C13	120.5 (5)	121.3 (2)
C12—C13—C14	120.7 (5)	119.4 (3)
C13—C14—C15	118.9 (5)	119.8 (3)
C14—C15—C16	120.5 (6)	120.4 (2)
C11—C16—C15	120.9 (5)	120.7 (2)
C12—C11—C2	121.5 (4)	120.2 (2)
C16—C11—C2	120.0 (4)	121.4 (2)
C01—C2—C11	110.8 (3)	112.8 (2)
C2—C3—C4	101.4 (4)	101.0 (2)
C01—C2—C3	111.1 (4)	108.7 (2)
C2—C3—O12	107.1 (4)	110.3 (2)
C11—C2—C3	112.7 (3)	114.8 (2)
C3—C4—C5	103.2 (4)	101.5 (2)
C01—C2—O11	110.2 (3)	108.7 (2)
C4—C3—O12	111.3 (3)	111.8 (2)

C11—C2—O11	108.6 (4)	107.2 (2)
C4—C5—O11	105.6 (4)	106.2 (2)
C3—C2—O11	103.1 (3)	104.2 (1)
C4—C5—C6	114.4 (4)	112.2 (2)
C2—O11—C5	110.2 (3)	109.8 (2)
C6—C5—O11	107.9 (4)	109.6 (2)
C5—C6—I	109.3 (3)	
C5—C6—N7		116.5 (2)
C6—N7—C8		110.0 (2)
C6—N7—C9		110.7 (2)
C6—N7—C10		106.4 (2)
C8—N7—C9		110.8 (2)
C8—N7—C10		109.3 (2)
C9—N7—C10		109.6 (2)
C5—O11—C2—C3	25.2 (4)	15.5 (2)
O11—C2—C3—C4	−38.9 (4)	−35.1 (2)
C2—C3—C4—C5	38.0 (4)	40.6 (2)
C3—C4—C5—O11	−23.8 (4)	−32.7 (2)
C4—C5—O11—C2	−1.2 (4)	10.7 (2)
C2—O11—C5—C6	121.6 (4)	132.1 (2)
O11—C5—C6—*X*	175.3 (3) (*X* = I)	87.8 (2) (*X* = N7)

Hydrogen bond for (2)

A—*B*···*C*	*A*···*C*	*B*···*C*	*A*—*B*···*C*
O12—H012···I^{i}	3.416 (2)	2.50 (4)	153 (3)

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

Table 3. *Pseudorotational parameters* (°) *for all published muscarine ions and compounds* (1) *and* (2)

The pseudorotational parameters were calculated by *PLATON* (Spek, 1991) according to the method described by Rao, Westhof & Sundaralingam (1981).

Compound	Phase	Amplitude	*T* – *E*
(1)	340.5 (4)	40.8 (3)	E_3
(2)	356.8 (2)	41.5 (1)	$^4T_3$
MUSCAI[a]	31.6	26.6	$^4T_5$
MUSCHL[b]	169.6 (1)	39.2 (1)	^3E
MUSPIC[c]	−5.7 (1)	41.5 (1)	$^4T_3$
MUSTPB[d]	0 (2)	36.3 (9)	$^4T_3$

Notes: (*a*) muscarine iodide (Jellinek, 1957); (*b*) muscarine chloride (Frydenvang & Jensen, 1990); (*c*) muscarine picrate (Frydenvang & Jensen, 1993); (*d*) muscarine tetraphenylborate (Frydenvang & Jensen, 1993).

Single crystals of (1) were obtained from a solution of the compound in 2-propanol. Single crystals of compound (2) were obtained by vapour diffusion of dimethoxymethane into a solution of the compound in methanol. The parameters of the benzene-ring H atoms in (1) and the H atoms of the aromatic rings and the quaternary ammonium group in (2) were not refined. Only the coordinates of the remaining H atoms were refined. In (2), high difference electron density is observed close to the iodide ion. Data reduction: *SDP BEGIN* (B. A. Frenz & Associates, Inc., 1982). Program(s) used to solve structure: *SDP PATTERSON*, *DIRDIF*. Program(s) used to refine structure: *SDP LSFM*. Molecular graphics: *ORTEP* (Johnson, 1976).

The two compounds were kindly donated by Dr M. De Amici, University of Milano, Italy.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71300 (61 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1063]

References

Angeli, P., Gianella, M., Pigini, M., Gualtieri, F., Teodori, E., Valsecchi, B. & Gaviraghi, G. (1986). *Eur. J. Med. Chem. Chim. Ther.* **20**, 517-523.

B. A. Frenz & Associates, Inc. (1982). *SDP Structure Determination Package*. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.

Dhanens, M., Lacombe, L., Lehn, J.-M. & Vigneron, J.-P. (1984). *J. Chem. Soc. Chem. Commun.* pp. 1097-1099.

Frydenvang, K. (1989). PhD thesis, Royal Danish School of Pharmacy, Copenhagen, Denmark.

Frydenvang, K. & Jensen, B. (1990). *Acta Cryst.* C**46**, 1279-1282.

Frydenvang, K. & Jensen, B. (1993). *Acta Cryst.* C**49**, 985-990.

Jellinek, F. (1957). *Acta Cryst.* **10**, 277-280.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Rao, S. T., Westhof, E. & Sundaralingam, M. (1981). *Acta Cryst.* A**37**, 421-425.

Spek, A. L. (1991). *PLATON*. Univ. of Utrecht, The Netherlands.

Acta Cryst. (1993). C**49**, 1840–1844

Structure of the Charge-Transfer Complexes 2,4,5,7-Tetranitro-9-fluorenone–1-Ethylnaphthalene (1/1) (I) and 2,4,5,7-Tetranitro-9-fluorenone–3,6-Dimethylphenanthrene (1/1) (II)

Steven L. Baldwin and Russell G. Baughman*

Division of Science, Northeast Missouri State University, Kirksville, MO 63501, USA

(*Received* 8 *June* 1992; *accepted* 8 *March* 1993)

Abstract

In each structure the asymmetric unit consists of two molecules whose parallel rings are at van der Waals distances and stack, alternately, along the *a* axis for (I) and along the *n*-glide direction for (II). The carbon-skeleton geometry of the fluorenone within both charge-transfer complexes is not significantly altered from that of the parent 2,4,5,7-tetranitro-9-fluorenone.

Comment

As a continuation of a study in this laboratory of a series of π–π^* charge-transfer complexes (Baughman, 1982, 1987; Shah & Baughman, 1993), the charge-transfer complexes of 2,4,5,7-tetranitro-9-fluorenone (TNF) with 1-ethylnaphthalene (1-ETNP) and 3,6-dimethylphenanthrene (3,6-DMP) were investigated. As a result of somewhat high *B* values for C24 and C25 in TNF:1-ETNP, a separate

Acta Crystallographica Section C
ISSN 0108-2701 ©1993