C(2)—N(3)—C(13)	120.0 (3)	C(14)—C(15)—C(16)	121.2 (3)
C(4)—N(3)—C(13)	120.7 (3)	C(15)—C(16)—C(17)	119.7 (3)
N(3)—C(4)—C(5)	122.3 (3)	C(16)—C(17)—C(18)	120.3 (3)
N(3)—C(4)—N(9)	125.7 (3)	C(16)—C(17)—N(21)	120.4 (3)
C(5)—C(4)—N(9)	112.1 (3)	C(18)—C(17)—N(21)	119.3 (3)
C(4)—C(5)—C(6)	123.2 (3)	C(17)—C(18)—C(19)	120.2 (3)
C(4)—C(5)—N(7)	105.4 (3)	C(14)—C(19)—C(18)	120.1 (3)
C(6)—C(5)—N(7)	131.3 (3)	C(17)—N(21)—O(22)	118.3 (3)
N(1)—C(6)—C(5)	111.2 (3)	C(17)—N(21)—O(23)	119.1 (3)
N(1)—C(6)—O(12)	121.5 (3)	O(22)—N(21)—O(23)	122.6 (4)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N(7)—H(7)···N(9^{i})	1.76 (3)	2.766 (4)	171 (3)
N(20)—H(20*B*)···O(10)	1.91 (4)	2.897 (4)	163 (3)
N(20)—H(20*A*)···O(22^{ii})	2.31 (4)	3.072 (4)	132 (3)
C(8)—H(8)···O(12^{iii})	2.30 (4)	3.247 (4)	149 (2)
C(15)—H(15)···O(23^{iv})	2.45 (3)	3.218 (4)	131 (2)

Symmetry codes: (i) $-1-x, \frac{1}{2}+y, -\frac{1}{2}-z$; (ii) $x, 1+y, z$; (iii) $-1-x, y-\frac{1}{2}, -\frac{1}{2}-z$; (iv) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *MULTAN*88 (Main *et al.*, 1988). Program(s) used to refine structure: *KPPXRAY* (Taga, Masuda, Higashi & Iizuka, 1991) including a modified version of *ORFLS* (Busing, Martin & Levy, 1962). Molecular graphics: *KPPXRAY*. Software used to prepare material for publication: *EDCIF-J* (Osaki & Taga, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 2392–2395

α- and γ-Polymorphs of Dimethyl 9-Chloromethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

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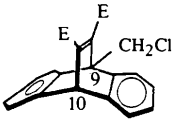
Abstract

Two further polymorphic forms (α = $P2_1$ and γ = $P2_1/c$) of the title compound ($C_{21}H_{17}ClO_4$) have been obtained and their crystal structures determined. The molecular geometries and photochemical behaviour are very similar to those of the previously described β-form reported in the $P2_1/c$ space group [Chen, Pokkuluri, Scheffer & Trotter (1993). *Acta Cryst.* B**49**, 905–909].

Comment

The crystal structure and photochemistry of the title compound have been described previously (Chen, Pokkuluri, Scheffer & Trotter, 1991, 1993). Further study of the material (Chen, 1991) led to isolation of two other polymorphic modifications. Crystallization from chloroform/methanol gives the previously described prismatic crystals (now named the β-form). Crystallization from diethyl ether/petroleum ether gives needles (α-form) and prisms (β-form), while crystallization from acetone/hexane gives block-shaped crystals (γ-form). The α-form has a melting point 6 K higher than the other two forms, and the three forms have slightly different FTIR (Fourier transform infrared) spectra and photochromic behaviour (Chen, 1991).



E = CO_2Me
(I)

The molecules in all three polymorphic forms have very similar conformations and dimensions (Table 2). The ester group remote from the chloromethyl substituent is conjugated with the C11=C12 double bond in each molecule; the C11—C12—C15—O4 torsion angles are not far from 0 or 180°, with $\cos^2$(angle) = 0.88–1.00 (0.67 for the disordered group of the γ-form). The ester group adjacent to the chloromethyl group is not conjugated, presumably as a result of steric interactions; the

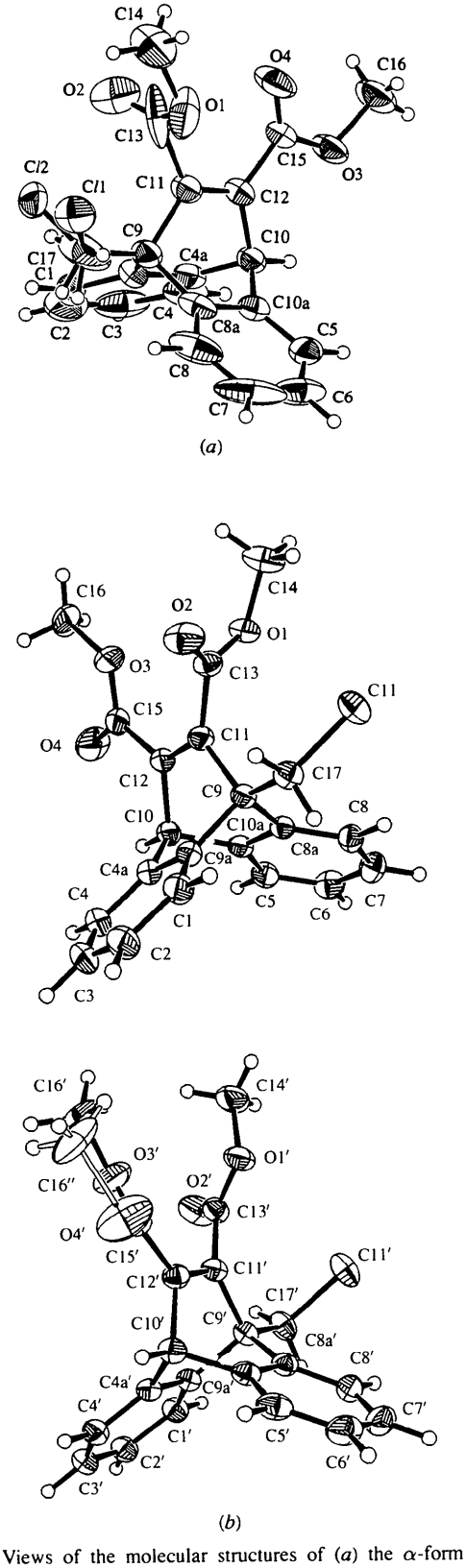


Fig. 1. Views of the molecular structures of (*a*) the α-form (50% ellipsoids) and (*b*) the two independent molecules of the γ-form (33% ellipsoids).

C12—C11—C13—O2 torsion angles are not far from 90°; $\cos^2$(angle) = 0.01–0.17. The C—CO_2Me distances in the α- and γ-forms reflect these differences, the non-conjugated distances being marginally longer than the conjugated distances (Table 2).

The photochemical behaviour of the α- and γ-forms is very similar to that of the β-form (Chen *et al.*, 1991), with only slight differences in the relative amounts of the four photoproducts.

Experimental

The polymorphs were synthesized by the method of Chen (1991).

α-Form

Crystal data

$C_{21}H_{17}ClO_4$
M_r = 368.82
Monoclinic
$P2_1$
a = 8.634 (1) Å
b = 8.863 (2) Å
c = 11.745 (1) Å
β = 98.33 (1)°
V = 889.3 (5) Å^3
Z = 2
D_x = 1.377 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 24 reflections
θ = 23–27°
μ = 2.1 mm^{-1}
T = 294 K
Needle
0.40 × 0.15 × 0.05 mm
Colourless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.33, T_{max} = 1.00
2056 measured reflections
1936 independent reflections

1322 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.014
θ_{max} = 77.5°
h = 0 → 11
k = 0 → 11
l = −15 → 15
3 standard reflections monitored every 250 reflections
intensity decay: 3.4%

Refinement

Refinement on F
R = 0.079
wR = 0.088
S = 4.6
1322 reflections
245 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.04
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Extinction correction: *TEXSAN* (Molecular Structure Corporation, 1985)
Extinction coefficient: 0.95 × 10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

γ-Form

Crystal data

$C_{21}H_{17}ClO_4$
M_r = 368.82

Cu $K\alpha$ radiation
λ = 1.5418 Å

Monoclinic
$P2_1/c$
a = 20.550 (1) Å
b = 10.513 (1) Å
c = 17.813 (1) Å
β = 108.11 (1)°
V = 3658 (1) Å^3
Z = 8
D_x = 1.339 Mg m^{-3}

Cell parameters from 25 reflections
θ = 48–51°
μ = 2.1 mm^{-1}
T = 294 K
Block
0.45 × 0.37 × 0.30 mm
Colourless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (*TEXSAN*; Molecular Structure Corporation, 1985)
T_{min} = 0.84, T_{max} = 1.00
7802 measured reflections
7537 independent reflections

5761 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.040
θ_{max} = 77.5°
$h = -25 \rightarrow 24$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 21$
3 standard reflections monitored every 200 reflections
intensity decay: 10.0%

Refinement

Refinement on F
R = 0.048
wR = 0.056
S = 4.0
5761 reflections
480 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.17
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Extinction correction: *TEXSAN* (Molecular Structure Corporation, 1985)
Extinction coefficient: 0.16 × 10^{-5}
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)

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

	x	y	z	U_{eq}
α-Form				
Cl1†	0.4902 (6)	0.5473	0.8194 (5)	0.105 (4)
Cl2‡	0.6555 (7)	0.558 (1)	0.8990 (5)	0.098 (4)
O1	0.610 (2)	0.636 (1)	0.5963 (8)	0.174 (8)
O2	0.830 (1)	0.627 (1)	0.7079 (10)	0.163 (9)
O3	0.789 (1)	1.128 (1)	0.5451 (6)	0.094 (5)
O4	0.800 (1)	0.889 (1)	0.5105 (6)	0.136 (6)
C1	0.776 (2)	0.913 (2)	1.0207 (8)	0.114 (8)
C2	0.880 (2)	1.017 (3)	1.0793 (10)	0.152 (12)
C3	0.910 (1)	1.144 (2)	1.0301 (10)	0.119 (10)
C4	0.837 (1)	1.187 (1)	0.9197 (9)	0.090 (6)
C4a	0.734 (1)	1.084 (1)	0.8623 (6)	0.068 (5)
C5	0.354 (1)	1.182 (1)	0.7189 (7)	0.092 (6)
C6	0.203 (1)	1.142 (3)	0.7381 (10)	0.137 (11)
C7	0.170 (2)	1.012 (3)	0.7821 (10)	0.165 (12)
C8	0.291 (1)	0.910 (2)	0.8146 (10)	0.125 (9)
C8a	0.444 (1)	0.944 (1)	0.8018 (7)	0.077 (5)
C9	0.592 (1)	0.845 (1)	0.8320 (7)	0.071 (5)
C9a	0.705 (1)	0.946 (1)	0.9099 (7)	0.080 (6)
C10	0.645 (1)	1.104 (1)	0.7410 (6)	0.066 (5)
C10a	0.475 (1)	1.081 (1)	0.7535 (6)	0.065 (5)
C11	0.663 (1)	0.836 (1)	0.7186 (7)	0.067 (5)
C12	0.691 (1)	0.971 (1)	0.6731 (6)	0.060 (4)
C13	0.708 (2)	0.690 (2)	0.6684 (10)	0.109 (9)
C14	0.696 (2)	0.489 (2)	0.5561 (10)	0.177 (12)
C15	0.764 (1)	0.987 (1)	0.5681 (7)	0.067 (5)
C16	0.856 (2)	1.157 (2)	0.4401 (10)	0.127 (9)
C17	0.563 (2)	0.699 (2)	0.8849 (10)	0.177 (12)
γ-Form				
Cl1	0.46467 (3)	0.14928 (6)	0.14386 (3)	0.0589 (4)
O1	0.56324 (8)	0.3959 (2)	0.17216 (9)	0.047 (1)
O2	0.6313 (1)	0.2303 (2)	0.1689 (1)	0.071 (1)
O3	0.6940 (1)	0.4666 (2)	0.2923 (1)	0.071 (1)
O4	0.7002 (1)	0.5038 (2)	0.4172 (1)	0.087 (1)
C1	0.6171 (1)	−0.0527 (2)	0.3630 (2)	0.053 (1)
C2	0.6632 (1)	−0.1082 (3)	0.4292 (2)	0.067 (1)
C3	0.6953 (1)	−0.0375 (3)	0.4948 (2)	0.066 (1)
C4	0.6822 (1)	0.0923 (3)	0.4967 (1)	0.057 (1)
C4a	0.6363 (1)	0.1484 (2)	0.4313 (1)	0.044 (1)
C5	0.5012 (1)	0.3450 (2)	0.4474 (1)	0.049 (1)
C6	0.4305 (1)	0.3351 (3)	0.4231 (2)	0.057 (1)
C7	0.3971 (1)	0.2665 (3)	0.3559 (2)	0.056 (1)
C8	0.4341 (1)	0.2069 (2)	0.3121 (1)	0.045 (1)
C8a	0.5044 (1)	0.2175 (2)	0.3358 (1)	0.037 (1)
C9	0.5545 (1)	0.1562 (2)	0.2973 (1)	0.038 (1)
C9a	0.6040 (1)	0.0770 (2)	0.3645 (1)	0.041 (1)
C10	0.6151 (1)	0.2879 (2)	0.4230 (1)	0.042 (1)
C10a	0.5379 (1)	0.2879 (2)	0.4036 (1)	0.039 (1)
C11	0.5984 (1)	0.2691 (2)	0.2837 (1)	0.041 (1)
C12	0.6303 (1)	0.3349 (2)	0.3493 (1)	0.043 (1)
C13	0.6012 (1)	0.2953 (2)	0.2024 (1)	0.045 (1)
C14	0.5539 (2)	0.4246 (3)	0.0903 (2)	0.072 (1)
C15	0.6782 (1)	0.4435 (3)	0.3574 (2)	0.053 (1)
C16	0.7421 (2)	0.5692 (4)	0.2957 (2)	0.092 (2)
C17	0.5227 (1)	0.0714 (2)	0.2261 (1)	0.045 (1)
Cl1′	0.02838 (4)	0.17087 (7)	0.35979 (4)	0.0695 (4)
O1′	0.15599 (9)	0.3883 (2)	0.3469 (1)	0.060 (1)
O2′	0.1915 (1)	0.1871 (2)	0.3454 (1)	0.080 (1)
O3′	0.2152 (1)	0.4256 (3)	0.2244 (1)	0.092 (1)
O4′	0.1397 (2)	0.5255 (3)	0.1300 (2)	0.128 (2)
C1′	0.0782 (1)	−0.0539 (2)	0.1540 (1)	0.047 (1)
C2′	0.0935 (1)	−0.1124 (2)	0.0912 (2)	0.053 (1)
C3′	0.0972 (1)	−0.0421 (3)	0.0280 (1)	0.053 (1)
C4′	0.0865 (1)	0.0887 (2)	0.0256 (1)	0.048 (1)
C4a′	0.0718 (1)	0.1476 (2)	0.0878 (1)	0.039 (1)
C5′	−0.0694 (1)	0.3560 (2)	0.0556 (1)	0.056 (1)
C6′	−0.1318 (1)	0.3457 (3)	0.0691 (2)	0.068 (1)
C7′	−0.1382 (1)	0.2736 (3)	0.1304 (2)	0.068 (1)
C8′	−0.0817 (1)	0.2103 (3)	0.1812 (2)	0.054 (1)
C8a′	−0.0186 (1)	0.2230 (2)	0.1687 (1)	0.041 (1)
C9′	0.0492 (1)	0.1572 (2)	0.2150 (1)	0.039 (1)
C9a′	0.0674 (1)	0.0763 (2)	0.1518 (1)	0.038 (1)
C10′	0.0571 (1)	0.2887 (2)	0.0950 (1)	0.043 (1)
C10a′	−0.0131 (1)	0.2942 (2)	0.1053 (1)	0.042 (1)
C11′	0.1037 (1)	0.2634 (2)	0.2352 (1)	0.041 (1)
C12′	0.1077 (1)	0.3308 (2)	0.1732 (1)	0.043 (1)
C13′	0.1551 (1)	0.2737 (2)	0.3152 (1)	0.048 (1)
C14′	0.2119 (2)	0.4101 (4)	0.4189 (2)	0.084 (2)
C15′	0.1546 (2)	0.4371 (3)	0.1728 (2)	0.067 (1)
C16′§	0.2572 (2)	0.5408 (5)	0.2318 (3)	0.092 (4)
C16′′¶	0.2168 (9)	0.605 (2)	0.158 (1)	0.10 (1)
C17′	0.0451 (1)	0.0766 (2)	0.2839 (1)	0.052 (1)

† Occupancy = 0.55.
‡ Occupancy = 0.45.
§ Occupancy = 0.76.
¶ Occupancy = 0.24.

Table 2. *Selected bond lengths* (Å) *and torsion angles* (°)

	α-Form	γ-Form
C=C	1.35 (1)	1.341 (3), 1.336 (3)
C—C(arom.)	1.31 (3)–1.41 (3)	1.368–1.401 (3)
C—CO_2Me	1.50 (2), 1.47 (2)	1.493 (3), 1.485 (3); 1.491 (3), 1.477 (3)
C—Cl	1.63 (2), 1.48 (2)	1.776 (2), 1.793 (3)
C12—C11—C13—O2	97 (1)	108.1 (3), −114.6 (3)
C11—C12—C15—O4	3 (1)	173.7 (3), −145.2 (3), 34.8 (4) (disorder)

The structure of the α-form was solved by a combination of Patterson and direct methods. The Cl atom is disordered over two sites; both sites were refined anisotropically, with their occupancies constrained to sum to unity (55 and 45%). All H atoms were included in calculated positions, with both sets of sites for the H atoms on the chloromethyl group included at the appropriate occupancies. An attempt was made to determine the chirality of the crystal studied, but refinement of the two enantiomorphs showed no significant differences in agreement factors. The high R factors probably result from the large overall thermal motion, which may be rationalized as a consequence of the disorder of the heaviest atom.

The structure of the γ-form was solved by direct methods. There are two molecules per asymmetric unit; one of the molecules exhibits disorder of one ester group.

For both compounds, data collection: *TEXSAN* (Molecular Structure Corporation, 1985); cell refinement: *TEXSAN*; data reduction: *TEXSAN*; program(s) used to solve structures: *TEXSAN*; program(s) used to refine structures: *TEXSAN*; molecular graphics: *TEXSAN*.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 2395–2397

1-Amino-2-nitro-4,5-bis(*p*-toluenesulfonamido)benzene

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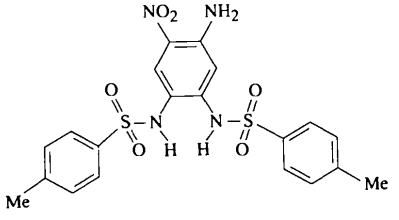
Abstract

The crystal structure of the title compound [alternative name: N,N'-(5-amino-4-nitrobenzene-1,2-diyl)bis(*p*-toluenesulfonamide)], $C_{20}H_{20}N_4O_6S_2$, has been determined. An intramolecular hydrogen bond between the amino and nitro groups keeps these groups nearly coplanar with the benzene ring.

Comment

The long-standing interest in substituted nitroanilines (Panunto, Urbanczyk-Lipowska, Johnson & Etter, 1987; Butcher, Gilardi, Flippen-Anderson & George, 1992) stems mainly from their large hyperpolarizabilities (Ledoux, Zyss, Siegel, Brienne & Lehn, 1990; Verbiest, Clays, Samyn, Wolff, Reinhoudt & Persoons, 1994), which makes them good candidates for non-linear optical studies. In the course of a study of 1,2,4,5-benzenetetramine derivatives, partial reduction of 1,2-dinitro-4,5-bis(*p*-tosylamido)benzene led to the title compound, (I), as a precursor of 1,2-diamino-4,5-bis(*p*-tosylamido)benzene.



(I)

Similar to most nitroanilines, the C—N bond length C(5)—N(8), involving the amino group, is shortened from a normal value of 1.428 Å to a value of 1.346 (4) Å, indicating significant double-bond character. However, a survey of *ortho*-nitroaniline structures in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) showed that the presence of tosylamido substituents causes this effect to be less pronounced than that observed for most other similar compounds [mean value of 1.325 (2) Å for 49 observed C—N_{amino} distances]. The amine proton H(82) is involved in intramolecular hydrogen bonding to the nitro O(72) atom with an O(72)···H(82) distance of 2.02 (4) Å. This keeps the nitro group in the benzene plane with an angle of rotation of 8.3°. The expected rotation angle for a nitro group having one substituent in an *ortho* position without hydrogen bonding is about 40° (Holden & Dickinson, 1969). For one of the tosylamido groups, the N(10) lone-pair direction is nearly perpendicular to the plane of the benzene ring (angle *ca* 74°), whereas for the other group, the N(20) lone pair is nearly parallel to this plane (angle *ca* 15°). This geometry increases the double-bond character of C(1)—N(10) as opposed to C(2)—N(20), with bond lengths of 1.401 (3) and 1.427 (3) Å, respectively. This effect is also reflected in the intracyclic C—C distances, the longest bonds, C(5)—C(4), C(5)—C(6) and C(1)—C(2), being those involving the C atoms

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