

O4	0.16711 (9)	-0.2700 (2)	0.25817 (10)	0.0403 (4)
O5	0.02444 (8)	0.2838 (2)	0.00527 (10)	0.0395 (4)
O6	0.11971 (9)	0.2419 (2)	-0.06356 (9)	0.0441 (4)
O7	0.12124 (10)	0.5138 (2)	0.10626 (11)	0.0428 (4)
O8	0.23660 (9)	0.4524 (2)	0.09227 (11)	0.0438 (4)
O9	0.09195 (7)	0.06570 (14)	0.27841 (8)	0.0235 (3)
O10	0.15906 (7)	0.26197 (14)	0.24155 (8)	0.0223 (3)
O11	0.07107 (7)	0.28425 (15)	0.33650 (8)	0.0260 (3)
N1	0.14015 (10)	-0.0979 (2)	0.07176 (10)	0.0261 (4)
N2	0.11884 (10)	-0.2052 (2)	0.20921 (10)	0.0251 (3)
N3	0.09059 (10)	0.2609 (2)	0.00106 (10)	0.0258 (3)
N4	0.17109 (10)	0.4265 (2)	0.09683 (10)	0.0269 (4)
F1	0.21429 (6)	-0.03382 (12)	0.20154 (7)	0.0272 (3)
F2	0.20568 (6)	0.18265 (12)	0.07850 (7)	0.0257 (3)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C1—O9	1.425 (2)	C4—F2	1.325 (2)
C1—C2	1.522 (3)	C5—O11	1.376 (2)
C1—C3	1.544 (2)	C5—O10	1.407 (2)
C2—F1	1.323 (2)	C5—O9	1.417 (2)
C3—O10	1.421 (2)	C6—O11	1.437 (2)
C3—C4	1.509 (2)		
O9—C1—C2	104.48 (14)	F2—C4—C3	115.43 (15)
O9—C1—C3	101.39 (13)	F2—C4—N3	108.14 (14)
C2—C1—C3	118.54 (15)	C3—C4—N3	113.01 (14)
F1—C2—C1	114.66 (15)	F2—C4—N4	107.47 (14)
F1—C2—N1	107.18 (13)	C3—C4—N4	108.81 (14)
C1—C2—N1	113.97 (14)	N3—C4—N4	103.14 (13)
F1—C2—N2	107.75 (14)	O11—C5—O10	112.45 (15)
C1—C2—N2	108.98 (14)	O11—C5—O9	105.72 (14)
N1—C2—N2	103.58 (13)	O10—C5—O9	106.45 (13)
O10—C3—C4	106.39 (14)	C5—O9—C1	109.44 (13)
O10—C3—C1	102.02 (13)	C5—O10—C3	104.22 (13)
C4—C3—C1	121.85 (14)	C5—O11—C6	113.0 (2)

Table 3. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the nitro groups with *e.s.d.*'s in parentheses and calculated standard deviations in square brackets

	Range	Mean
C—N	1.536 (2)–1.548 (2)	1.542 [5]
N—O	1.203 (2)–1.219 (2)	1.210 [5]
O—N—O	127.1 (2)–128.4 (2)	127.8 [5]
C—N—O	114.5 (2)–117.3 (2)	116 [1]

H atoms were refined in observed positions. One reflection (802) had an unusually large disagreement between  $F_o^2$  and  $F_c^2$  ( $10\sigma$ ) and was excluded from the final stages of refinement. The next largest disagreement was  $5.0\sigma$  and no other disagreements were larger than  $3.9\sigma$ . The highest peaks in the final difference map were attributable to bonding electrons between C atoms.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990a). Program(s) used to refine structure: SHELXTL (Sheldrick, 1990b).

Support from the Department of Chemistry of Georgetown University, Washington, DC, USA, is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BK1205). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Phase Transition and Expected Non-Linear Polarizability of 1-Hydroxy-4-(4-methylphenylamino)-9,10-anthraquinone

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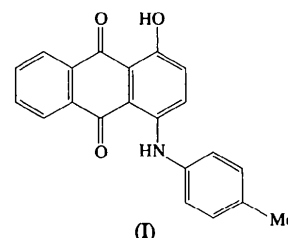
(Received 14 September 1995; accepted 15 January 1996)

## Abstract

The title compound,  $C_{21}H_{15}NO_3$ , shows a second-order phase transition above 313 K. Both phases are non-centrosymmetric. According to semi-empirical calculations, these polar crystals are liable to exhibit second-order hyperpolarizability.

## Comment

In the framework of our investigation of anthraquinone dyes, we studied 1-hydroxy-4-(4-methylphenylamino)-9,10-anthraquinone, (I), which is also known as Solvent Violet 13 or Disperse Blue 72.



The molecules of (I) form stacks along [100], with an interplanar distance of 3.50 Å. There are two independent molecules, 1 and 2, which have essentially the same conformation (the difference in torsion angles is less than 4°) and orientation (within 1°). Molecule 2 coincides with molecule 1 through vector shift (0.000, -0.019, 0.500), *i.e.* the structure contains pseudo-translation  $c/2$ . As a result, the reflections with odd  $l$  indices are much less intense than those with even  $l$  indices. The formation of a superlattice could be described as the shift of alternate molecules by 0.28 Å along the  $y$  axis. This type of ordering often results from a frozen-mode phase transition. The intensities of the strongest reflections with odd  $l$  indices decrease by a factor of 3.7–4.2 as the temperature increases from 291 to 298 K. At 303 and 313 K, only one such reflection ( $\bar{1}, 11, 9$ ) remains to be observed and at 333 K, all reflections with odd  $l$  indices are unobserved. At the same time, only a 1% loss in the intensities of the strong reflections with even  $l$  indices occurs and the volume thermal expansion is less than 0.7%. These variations indicate that the modulation along  $y$  decreases as the temperature increases and above 313 K becomes equal to zero, *i.e.* the second-order phase transition has taken place. The volume of the high-temperature unit cell is half that of the low-temperature one ( $clc' = 0.5$ ), but space group  $P2_1$  is retained.

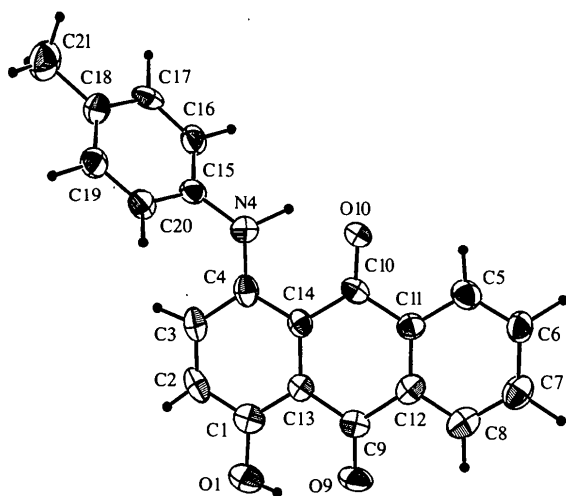


Fig. 1. ORTEP (Johnson, 1965) plot of molecule 1 of the title compound. The displacement ellipsoids are plotted at the 60% probability level.

In order to evaluate the potential polar and non-linear optical properties of crystals, semi-empirical computations of the electronic structure and polarizability with geometry optimization were carried out using the MOPAC6.0 package (Stewart, 1990). The calculations with full geometry optimization overestimate strongly the degree of the tricyclic distortion; the dihe-

dral angle formed by the terminal rings is 24° according AM1 calculations, 20° according to PM3 calculations and only 2° from X-ray data. The AM1 parametrization reproduces the conformation of the tolylamino group better than PM3; the observed, AM1-calculated and PM3-calculated torsion-angle values for C3—C4—N4—C15 are 11, 26 and 47°, respectively, and for C4—N4—C15—C16 are -140, -151 and -159°, respectively. Thus, we have concluded that PM3 underestimates the  $\pi$  conjugation of the amino group and quinonoid moiety, and the MNDO-AM1 Hamiltonian method has been used for further calculations. Moreover, the anthraquinone moiety (the tricycle with the O1, N4, O9 and O10 atoms) was considered to be planar and the two above mentioned torsion angles were fixed at their experimental values. Comparison of the experimental geometry with that obtained from semi-empirical calculations shows that the  $\pi$  conjugation in the keto-hydroxy and ketoamino cells is more considerable in the crystals than is evident from the calculations. The shortening of the N4—C4 bond relative to the N4—C15 bond is the most prominent; 0.052 (X-ray) and 0.027 Å (AM1).

The calculated dipole moment is almost normal to the long axis of the tricycle and forms an angle of 60° with the crystallographic  $y$  axis, *i.e.* the  $\mu_y$  component is equal to 1 D. The crystal field is supposed to increase the charge transfer along the tricycle axis simultaneously with the increase of  $\mu_y$ , so the crystal is liable to have permanent dipole properties. The direction of the largest molecular second-order hyperpolarizability  $\beta$  is almost coincident with the long axis and forms an angle of 75° with the dipole moment. The values of  $\beta$  in perpendicular directions are four times smaller and the value of  $\beta$  along the dipole moment is therefore only  $2.1 \times 10^{-30}$  e.s.u. The molecular packing is close to optimal and the largest of the non-linearity coefficients of the unit cell (per one molecule),  $b_{yyy}$ , is  $5.4 \times 10^{-30}$  e.s.u., *i.e.* 73% of the largest  $\beta$ .

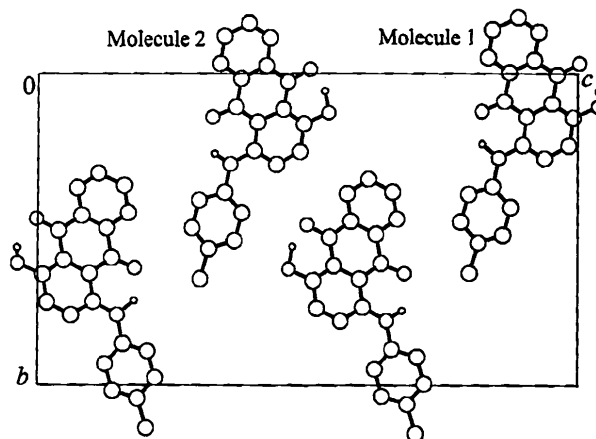


Fig. 2. Packing diagram viewed down the  $x$  axis.

**Experimental**

Crystals of (I) were grown from benzene and toluene solutions as flat needles. The largest dimension is coincident with [100] and the shortest with [001].

*Crystal data*C<sub>21</sub>H<sub>15</sub>NO<sub>3</sub>M<sub>r</sub> = 329.34

Monoclinic

P2<sub>1</sub>

a = 3.9160 (8) Å

b = 15.019 (3) Å

c = 26.479 (5) Å

β = 94.83 (2)°

V = 1551.8 (5) Å<sup>3</sup>

Z = 4

D<sub>x</sub> = 1.410 Mg m<sup>-3</sup>D<sub>m</sub> not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 22 reflections

θ = 14.9–16.7°

μ = 0.095 mm<sup>-1</sup>

T = 291 (2) K

Needle

0.8 × 0.3 × 0.07 mm

Blue-violet

*Data collection*

Enraf–Nonius CAD-4 four-circle diffractometer

Profile data from ω scans

Absorption correction: none

4990 measured reflections

2551 independent reflections

1248 observed reflections

[I &gt; 2σ(I)]

R<sub>int</sub> = 0.0491θ<sub>max</sub> = 23.98°

h = -4 → 4

k = -17 → 17

l = 0 → 30

3 standard reflections

frequency: 90 min

intensity decay: none

*Refinement*Refinement on F<sup>2</sup>

R(F) = 0.0420

wR(F<sup>2</sup>) = 0.0853

S = 0.888

2551 reflections

552 parameters

All H-atom parameters

refined, except for methyl

H atoms

w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0310P)<sup>2</sup>]where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3(Δ/σ)<sub>max</sub> = 0.112Δρ<sub>max</sub> = 0.163 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0.138 e Å<sup>-3</sup>

Extinction correction:

SHELXL93 (Sheldrick, 1992)

Extinction coefficient:

0.0107 (10)

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Absolute configuration:

Flack (1983) parameter = -0.6 (19)

C1A	0.0854 (19)	0.1628 (5)	0.4910 (3)	0.052 (2)
C2	-0.024 (2)	0.2312 (5)	0.9829 (3)	0.055 (2)
C2A	-0.0171 (19)	0.2508 (5)	0.4841 (3)	0.055 (2)
C3	0.0196 (19)	0.2729 (5)	0.9385 (3)	0.051 (2)
C3A	0.013 (2)	0.2919 (5)	0.4396 (3)	0.060 (3)
C4	0.1634 (18)	0.2294 (4)	0.8981 (3)	0.047 (2)
C4A	0.1546 (18)	0.2474 (4)	0.3984 (2)	0.049 (2)
C5	0.632 (2)	-0.0523 (5)	0.8341 (3)	0.055 (2)
C5A	0.6371 (19)	-0.0327 (5)	0.3346 (3)	0.055 (2)
C6	0.730 (2)	-0.1399 (4)	0.8416 (3)	0.052 (2)
C6A	0.731 (2)	-0.1188 (6)	0.3426 (3)	0.065 (3)
C7	0.701 (2)	-0.1794 (5)	0.8889 (3)	0.058 (2)
C7A	0.706 (2)	-0.1604 (6)	0.3884 (4)	0.074 (3)
C8	0.569 (2)	-0.1318 (5)	0.9274 (3)	0.058 (2)
C8A	0.579 (2)	-0.1137 (5)	0.4273 (3)	0.058 (2)
C9	0.3266 (17)	0.0042 (4)	0.9614 (3)	0.042 (2)
C9A	0.326 (2)	0.0254 (5)	0.4609 (3)	0.060 (3)
C10	0.3927 (16)	0.0895 (4)	0.8641 (2)	0.039 (2)
C10A	0.396 (2)	0.1077 (4)	0.3643 (3)	0.059 (3)
C11	0.4999 (18)	-0.0038 (4)	0.8734 (3)	0.042 (2)
C11A	0.5055 (19)	0.0157 (4)	0.3738 (3)	0.050 (2)
C12	0.4725 (19)	-0.0435 (4)	0.9193 (3)	0.048 (2)
C12A	0.4711 (18)	-0.0258 (5)	0.4209 (3)	0.050 (2)
C13	0.2224 (17)	0.0970 (4)	0.9520 (2)	0.038 (2)
C13A	0.219 (2)	0.1151 (5)	0.4525 (3)	0.052 (2)
C14	0.2581 (17)	0.1396 (4)	0.9050 (2)	0.040 (2)
C14A	0.2563 (17)	0.1574 (4)	0.4047 (2)	0.045 (2)
C15	0.1560 (17)	0.3633 (4)	0.8429 (2)	0.045 (2)
C15A	0.1520 (19)	0.3823 (4)	0.3436 (3)	0.055 (2)
C16	-0.0075 (19)	0.3879 (4)	0.7979 (3)	0.050 (2)
C16A	-0.011 (2)	0.4069 (5)	0.2967 (3)	0.057 (2)
C17	-0.0282 (19)	0.4760 (5)	0.7835 (2)	0.049 (2)
C17A	-0.025 (2)	0.4955 (5)	0.2834 (4)	0.067 (3)
C18	0.108 (2)	0.5424 (4)	0.8160 (3)	0.053 (2)
C18A	0.113 (2)	0.5619 (5)	0.3144 (3)	0.059 (3)
C19	0.2656 (19)	0.5182 (4)	0.8615 (3)	0.049 (2)
C19A	0.269 (2)	0.5360 (5)	0.3618 (3)	0.060 (2)
C20	0.2945 (18)	0.4298 (4)	0.8756 (3)	0.049 (2)
C20A	0.288 (2)	0.4479 (5)	0.3757 (3)	0.060 (2)
C21	0.082 (2)	0.6390 (5)	0.7994 (3)	0.078 (3)
C21A	0.090 (2)	0.6574 (5)	0.2987 (3)	0.082 (3)

Table 2. Selected geometric parameters (Å, °)

O1—C1	1.350 (7)	C2A—C3A	1.345 (9)
O1A—C1A	1.359 (7)	C3—C4	1.410 (9)
O9—C9	1.236 (7)	C3A—C4A	1.430 (9)
O9A—C9A	1.273 (8)	C4—C14	1.405 (8)
O10—C10	1.229 (7)	C4A—C14A	1.415 (9)
O10A—C10A	1.256 (8)	C9—C13	1.467 (9)
N4—C4	1.353 (8)	C9—C12	1.480 (10)
N4—C15	1.420 (8)	C9A—C13A	1.422 (10)
N4A—C4A	1.363 (8)	C9A—C12A	1.462 (11)
N4A—C15A	1.401 (9)	C10—C14	1.454 (9)
C1—C13	1.389 (9)	C10—C11	1.477 (9)
C1—C2	1.406 (10)	C10A—C14A	1.449 (10)
C1A—C13A	1.382 (9)	C10A—C11A	1.462 (10)
C1A—C2A	1.389 (10)	C14—C13	1.416 (9)
C2—C3	1.356 (9)	C14A—C13A	1.437 (9)
C4—N4—C15	127.4 (6)	N4A—C4A—C3A	120.2 (7)
C4A—N4A—C15A	128.7 (6)	O9—C9—C13	122.3 (6)
O1—C1—C13	124.0 (6)	O9—C9—C12	120.9 (6)
O1—C1—C2	117.1 (6)	O9A—C9A—C13A	122.1 (7)
O1A—C1A—C13A	122.0 (7)	O9A—C9A—C12A	116.9 (7)
O1A—C1A—C2A	116.6 (6)	O10—C10—C14	122.5 (6)
N4—C4—C14	120.8 (6)	O10—C10—C11	118.5 (6)
N4—C4—C3	121.6 (7)	O10A—C10A—C14A	122.1 (7)
N4A—C4A—C14A	121.2 (6)	O10A—C10A—C11A	118.9 (7)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

	$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$			
	x	y	z	$U_{eq}$
O1	0.0452 (15)	0.1073 (3)	1.0371 (2)	0.074 (2)
O1A	0.0449 (14)	0.1261 (4)	0.5370 (2)	0.074 (2)
O9	0.2946 (15)	-0.0332 (3)	1.0023 (2)	0.066 (2)
O9A	0.2929 (16)	-0.0145 (3)	0.5026 (2)	0.072 (2)
O10	0.4268 (13)	0.1222 (3)	0.8223 (2)	0.061 (2)
O10A	0.4177 (15)	0.1403 (3)	0.3210 (2)	0.074 (2)
N4	0.2024 (17)	0.2714 (3)	0.8537 (2)	0.059 (2)
N4A	0.1847 (17)	0.2911 (4)	0.3538 (2)	0.061 (2)
C1	0.0850 (18)	0.1428 (4)	0.9911 (3)	0.049 (2)

Although the contributions of reflections with odd *l* indices to the disagreement factors were smaller than those with even *l* indices, the values of *S* calculated for the *l* even and the *l* odd classes of reflections were 1.15 and 0.92, respectively. Thus, it was concluded that the structural model represents

the formation of the supercell adequately. Methyl H atoms were considered as part of idealized tetrahedral groups. The enantiomorphs are indistinguishable from the X-ray data.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL93* and *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data, torsion angles, temperature-induced changes in reflection intensities, *AM1* and *PM3* geometry optimization, *AM1* calculations of geometry and polarizability, and finite-field polarizabilities have been deposited with

the IUCr (Reference: KA1165). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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