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A 2:1 complex of 1,3-bis(9*H*-carbazol-9-yl)propane and tetrachloro-*p*-benzoquinone (*p*-chloranil)Mustafa Arslan,^{a*} Erol Asker,^b
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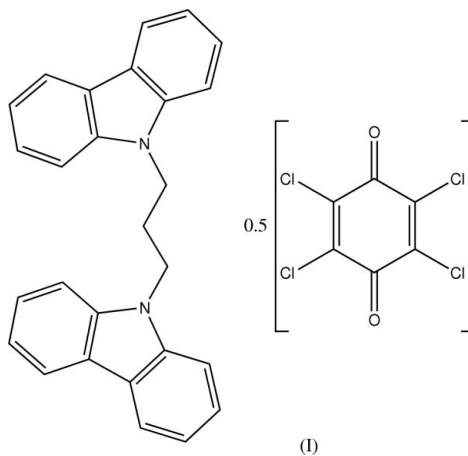
Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(C-C)$ = 0.003 Å
R factor = 0.040
wR factor = 0.097
Data-to-parameter ratio = 13.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

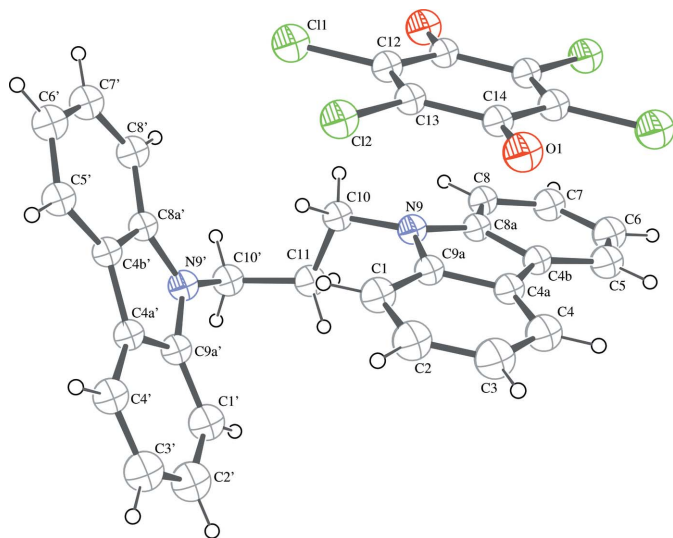
In the title electron donor–acceptor complex, $C_{27}H_{22}N_2 \cdot 0.5C_6Cl_4O_2$, the *p*-chloranil molecule lies on a crystallographic inversion center, which is located at the center of the benzene ring. In the crystal structure, one *p*-chloranil molecule lies above and below the central rings of each donor group of two neighboring 1,3-bis(9*H*-carbazol-9-yl)propane molecules, with a ring-centroid separation of 3.444 (1) Å. The angle between the planes of the stacking rings of the carbazole and *p*-chloranil molecules is 3.4 (2)°.

Comment

Electron donor–acceptor (EDA) complexes of carbazoles with certain electron acceptors have attracted much interest, due to their application in industry as photoconductors (Sirotkina *et al.*, 1985; Haderski *et al.*, 2000; Tazuke & Nagahara, 2003). The addition of various electron acceptors as dopants to polyvinylcarbazole (PVK) increases the photosensitivity of these materials in the visible region. Studies of the EDA complexes of some low molecular weight examples of PVK have been conducted in order to understand the nature of the complexation both in solution and in the solid state. We report here the results of the single-crystal X-ray diffraction analysis of an EDA complex of 1,3-bis(9*H*-carbazol-9-yl)propane and *p*-chloranil, (I), carried out to determine the intermolecular relations, molecular geometry, and stoichiometry of complexation.



Complex (I) crystallizes as a 2:1 complex, with a donor:–acceptor ratio of 4:1. The asymmetric unit contains one 1,3-bis(9*H*-carbazol-9-yl)propane molecule and one half of a *p*-chloranil molecule. The other half of the *p*-chloranil molecule is generated by a crystallographic inversion center. The bond lengths and angles of the carbazolyl rings and the *p*-chloranil


Figure 1

The structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabeled atoms of *p*-chloranil are related to labeled atoms by the symmetry operator $(1 - x, -y, 1 - z)$.

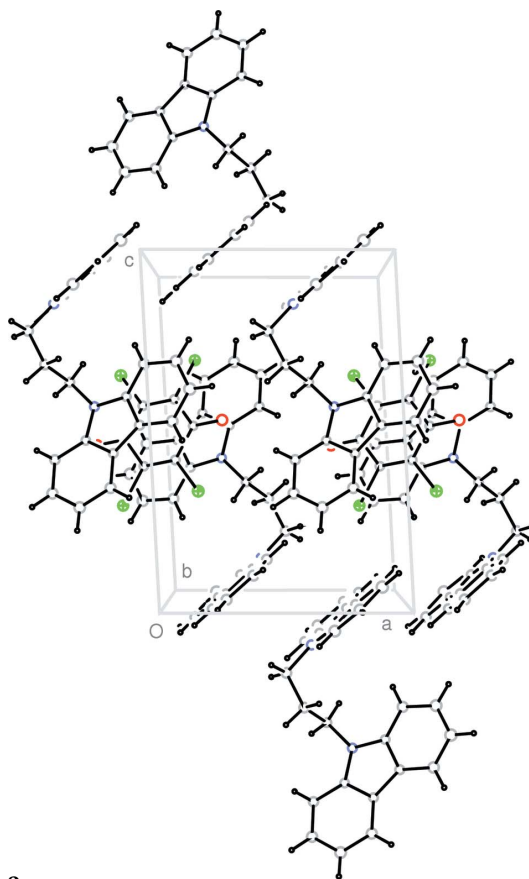
molecule in the complex do not deviate significantly from those of related compounds reported in the literature (Chu *et al.*, 1962; Baker *et al.*, 1991; Duan *et al.*, 2004; Wang *et al.*, 2006).

Each of the carbazole skeletons and the *p*-chloranil molecule in (I) (Fig. 1) are essentially planar, with r.m.s deviations of 0.056 (unprimed ring), 0.008 (primed ring) and 0.007 Å (*p*-chloranil). The dihedral angle between the planes of the carbazole ring systems is 52.52 (9)°. The methylene chain connecting the two carbazole groups exhibits an *anti-gauche* conformation.

The molecular packing of (I) (Fig. 2) is mainly determined by π - π interactions between the central ring of the carbazole group and the *p*-chloranil ring. One *p*-chloranil molecule associates with two centrosymmetrically related neighboring carbazole rings, forming a sandwich-type complex. The dihedral angles between the mean planes of the *p*-chloranil ring at (x, y, z) and the pyrrole rings of each of the neighboring dicarbazolyl molecules at (x, y, z) and $(1 - x, -y, 1 - z)$ are equal [3.4 (2)°], with ring-centroid separations of 3.444 (1) Å and interplanar spacings of *ca* 3.331 Å, corresponding to a ring-centroid offset of *ca* 0.875 Å. Additionally, the crystal structure is also stabilized by a C—H... π interaction involving the C4—H4 atoms of one molecule and the benzene ring of a second, with $H4 \cdots Cg^i = 2.81$ Å, where Cg is the centroid of the C4b/C5—C8/C8a ring [symmetry code: (i) $x, \frac{1}{2} - y, -\frac{1}{2} + z$].

Experimental

1,3-Bis(9*H*-carbazol-9-yl)propane was synthesized from the potassium salt of carbazole and 1,3-dibromopropane according to the literature procedure of Ohline *et al.* (1992). Dark-blue crystals of the EDA complex of 1,3-bis(9*H*-carbazol-9-yl)propane with *p*-chloranil were grown from a concentrated solution (1:1 molar ratio) in dichloromethane by slow evaporation at room temperature. Crystals


Figure 2

The crystal packing of (I), viewed down the *b* axis.

of the title compound were separated manually from the yellow crystals of uncomplexed *p*-chloranil.

Crystal data

$C_{27}H_{22}N_2 \cdot 0.5C_6Cl_4O_2$
 $M_r = 497.42$
 Monoclinic, $P2_1/c$
 $a = 12.9035$ (11) Å
 $b = 20.8191$ (15) Å
 $c = 9.0126$ (7) Å
 $\beta = 93.05$ (7)°
 $V = 2417.7$ (4) Å³

$Z = 4$
 $D_x = 1.367$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.30$ mm⁻¹
 $T = 295$ (2) K
 Prism, dark blue
 $0.46 \times 0.37 \times 0.33$ mm

Data collection

Enraf–Nonius CAD-4
 diffractometer
 ω scans
 Absorption correction: none
 4289 measured reflections
 4289 independent reflections

3045 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 25.1^\circ$
 2 standard reflections
 frequency: 120 min
 intensity decay: 0.7%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.097$
 $S = 1.02$
 4289 reflections
 316 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.8023P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.15$ e Å⁻³
 $\Delta\rho_{\min} = -0.18$ e Å⁻³

All H atoms were positioned geometrically and allowed to ride on their parent atoms with C—H distances of 0.93 and 0.97 Å for

aromatic and methylene H atoms, respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC Software*; data reduction: *DATRD2* in *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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