C4a—C4b—C4c	112.03 (13)	C4a—C8e—C1	120.1 (2)
O1—C4b—C8c	116.67 (13)	C4a—C8e—C8d	110.1 (2)
C4a—C4b—C8c	104.3 (2)	C1—C8e—C8d	129.7 (3)
C4c—C4b—C8c	103.50 (13)	O3—C9—O10	111.9 (2)
C5—C4c—C8a	121.2 (2)	O3—C9—C17	111.3 (2)
C5—C4c—C4b	126.4 (2)	O10—C9—C17	107.5 (2)
C8a—C4c—C4b	112.4 (2)	O3—C9—C8b	104.7 (2)
C4c—C8a—C8b	111.90 (14)	O10—C9—C8b	104.9 (2)
C8—C8a—C8b	129.0 (2)	C17—C9—C8b	116.4 (2)
C8a—C8b—C9	116.4 (2)	O4—C10—C11	118.40 (15)
C8a—C8b—C8c	104.93 (15)	O4—C10—C8c	118.11 (14)
C9—C8b—C8c	103.8 (2)	C11—C10—C8c	123.45 (14)
C10—C8c—C8d	114.40 (15)	C18—C17—C9	121.2 (2)
C10—C8c—C8b	112.37 (13)	C22—C17—C9	119.4 (2)
C8d—C8c—C8b	103.5 (2)		

Crystals of appropriate dimensions of both (3) and (5) were mounted on glass fibers in random orientations. Auto-indexing of ten centered reflections from the rotation photograph indicated a monoclinic lattice for (3) and an orthorhombic lattice for (5). Axial photographs were taken to confirm the Laue symmetry and cell lengths. Intensity data were collected with a variable scan speed. Data reduction, structure solution and structure refinement were carried out using the *SHELXTL-Plus* software package (Sheldrick, 1995). The structures were solved by direct methods. Full-matrix least-squares refinement minimized $w(F_o^2-F_c^2)^2$. The non-H atoms were refined anisotropically to convergence. All H atoms were refined using an appropriate riding model.

For both compounds, data collection: *P*3 (Siemens, 1990); cell refinement: *P*3; data reduction: *XDISK* in *SHELXTL Plus* (Sheldrick, 1995); program(s) used to solve structures: *SHELXTL-Plus*; program(s) used to refine structures: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

The authors thank the Council of Scientific and Industrial Research, Government of India (SAK, TM, SD and MVG), the National Science Foundation, Department of Chemistry of the University of Missouri–St. Louis (NPR) and the Office of Basic Energy Sciences of the US Department of Energy (MVG) for financial support of this work. This is document No. NDRL 3736 from the ND Radiation Laboratory and No. RRLT-PRU 49 from the RRL (CSIR), Trivandrum.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Kumar, S. A., Asokan, C. V., Mathew, T., Ramaiah, D., Das, S., Rath, N. P. & George, M. V. (1996). *J. Org. Chem.* In the press.

Murty, B. A. R. C., Pratapan, S., Kumar, C. V., Das, P. K. & George, M. V. (1985). *J. Org. Chem.* **50**, 2533–2538.

Pratapan, S., Ashok, K., Gopidas, K. R., Rath, N. P., Das, P. K. & George, M. V. (1990). *J. Org. Chem.* **55**, 1304–1308.

Sheldrick, G. M. (1995). *SHELXTL-Plus. Program for the Solution and Refinement of Crystal Structures*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1990). *P3. A Crystallographic Data Collection Program*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). C**52**, 2800–2802

The Photoproduct Derived from 9-Cyanodibenzobarrelene

M. Muneer,[a] M. V. George[a,b] and Nigam P. Rath[c]

[a]*Regional Research Laboratory (CSIR), Trivandrum 695019, India,* [b]*Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA, and* [c]*Department of Chemistry, University of Missouri–St. Louis, 8001 Natural Bridge Road, St. Louis, MO 63121, USA. E-mail: nigam_rath@umsl.edu*

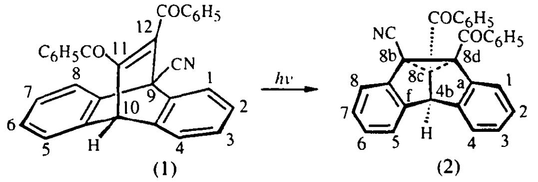
(*Received 25 July 1994; accepted 31 May 1996*)

Abstract

The structure of the photoproduct derived from 9-cyano-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene has been unambiguously established as 8b-cyano-8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydrodibenzo[*a*,*f*]cyclopropa[*c*,*d*]pentalene, $C_{31}H_{19}NO_2$, through X-ray crystallographic analysis.

Comment

It has been reported previously that dibenzobarrelenes containing the 1,2-dibenzoylalkene moiety undergo photorearrangement on irradiation to give predominantly the corresponding dibenzocyclopropapentalenes or products derived from them (Kumar, Murty, Lahiri, Chackacheri, Scaiano & George 1994; Murty, Pratapan, Kumar, Das & George, 1995; Pratapan, Ashok, Cyr, Das & George, 1987; Pratapan, Ashok, Gopidas, Rath, Das & George, 1990; Asokan, Kumar, Das, Rath & George, 1991; Kumar, Asokan, Das, Wilbur, Rath & George, 1993). If the dibenzobarrelenes have bridgehead substituents, then regioisomeric dibenzocyclopropapentalenes could be formed on irradiation. The regioselectivity in these rearrangements could, however, depend on several factors including the steric and electronic requirements of the bridgehead substituent. We have reported previously (Murty, Pratapan, Kumar, Das & George, 1995) that the photolysis of 9-cyano-11,12-dibenzoyl-9,10-dihydro-9,10-ethanoanthracene, (1), gives exclusively the title 8b-cyanosubstituted dibenzocyclopropapentalene, (2) and not the 4b-substituted regioisomer.



(1) (2)

In view of the recent report that dibenzocyclopropapentalenes containing three substituents attached to the cyclopropane ring show a propensity for ring enlargement (Pratapan, Ashok, Gopidas, Rath, Das & George, 1990), it became necessary to establish the structure of (2) unambiguously. This has now been achieved through single-crystal X-ray diffraction studies and it was found that the cyclopane ring in (2) is intact.

The molecular structure of (2) contains a 6,5,3,5,6-fused-ring system, shaped like a butterfly hanging down on both sides of the C4b—C8c bond. The 'butterfly angle' formed by the fusion of the two indane ring systems is 86.7 (7)°. The structure showed bond-angle and bond-distance values within the accepted range. All the phenyl rings in the structure are planar within experimental error. No close intermolecular non-bonded contacts were observed from the crystal packing.

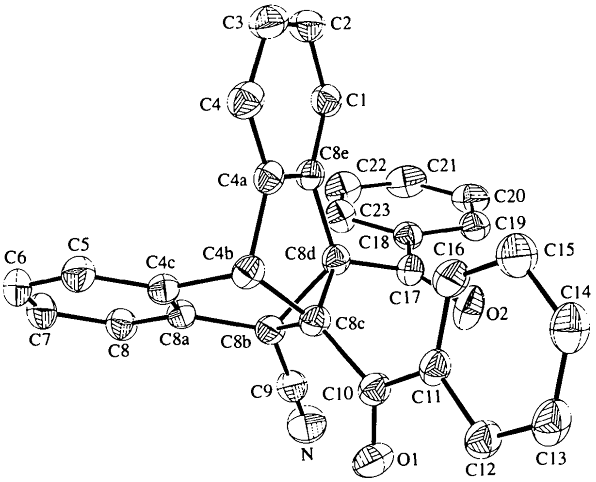


Fig. 1. View of (2) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 30% probability level.

Experimental

The title compound was prepared according to Murty, Pratapan, Kumar, Das & George (1985). Colorless rectangular crystals were obtained by slow evaporation of a solution of (2) in a 1:1 mixture of benzene and petroleum ether (b.p. 333–353 K) at room temperature (298 K).

Crystal data

$C_{31}H_{19}NO_2$
$M_r = 437.47$
Monoclinic
$P2_1/n$
$a = 9.078(2)$ Å
$b = 14.909(3)$ Å
$c = 16.576(3)$ Å
$\beta = 91.73(3)°$
$V = 2242.4(8)$ Å^3
$Z = 4$
$D_x = 1.296$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ graphite-monochromated radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 10.0–15.0°$
$\mu = 0.639$ mm^{-1}
$T = 298(2)$ K
Rectangular
0.30 × 0.30 × 0.30 mm
Colorless

Data collection

Siemens *P*4 diffractometer
ω–2θ scans
Absorption correction: none
3943 measured reflections
2969 independent reflections
2455 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0325$

$\theta_{\rm max} = 56.70°$
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 16$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 100 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0423$
$wR(F^2) = 0.1184$
$S = 1.304$
2951 reflections
307 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.057P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.127$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.188$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
O1	0.0850 (2)	0.94300 (10)	0.07783 (9)	0.0637 (4)
O2	0.3348 (2)	0.78629 (10)	0.11312 (10)	0.0682 (5)
N	−0.0374 (2)	0.7790 (2)	0.20924 (12)	0.0756 (6)
C1	0.2382 (2)	0.58254 (13)	−0.05034 (12)	0.0481 (5)
C2	0.2590 (2)	0.54931 (15)	−0.12697 (13)	0.0566 (6)
C3	0.2049 (3)	0.5930 (2)	−0.19460 (13)	0.0598 (6)
C4	0.1237 (2)	0.67161 (15)	−0.18692 (12)	0.0542 (6)
C4a	0.1050 (2)	0.70678 (13)	−0.11104 (11)	0.0427 (5)
C4b	0.0157 (2)	0.78803 (13)	−0.08573 (11)	0.0437 (5)
C4c	−0.1375 (2)	0.75190 (12)	−0.07033 (11)	0.0443 (5)
C5	−0.2544 (2)	0.73652 (14)	−0.12426 (13)	0.0548 (6)
C6	−0.3797 (2)	0.6949 (2)	−0.09635 (14)	0.0615 (6)
C7	−0.3866 (2)	0.6677 (2)	−0.01713 (15)	0.0614 (6)
C8	−0.2706 (2)	0.68272 (14)	0.03716 (13)	0.0522 (5)
C8a	−0.1466 (2)	0.72518 (12)	0.00971 (11)	0.0426 (5)
C8b	−0.0126 (2)	0.75429 (12)	0.05621 (11)	0.0417 (5)
C8c	0.0803 (2)	0.80965 (12)	0.00045 (11)	0.0416 (5)
C8d	0.1470 (2)	0.72218 (12)	0.02983 (11)	0.0399 (4)
C8e	0.1637 (2)	0.66325 (12)	−0.04245 (11)	0.0403 (5)
C9	−0.0256 (2)	0.77227 (14)	0.14103 (13)	0.0503 (5)
C10	0.1362 (2)	0.90259 (13)	0.02140 (12)	0.0454 (5)
C11	0.2483 (2)	0.94290 (13)	−0.03103 (12)	0.0458 (5)
C12	0.2790 (2)	1.03365 (14)	−0.02334 (13)	0.0545 (5)
C13	0.3872 (3)	1.07272 (15)	−0.06822 (15)	0.0624 (6)
C14	0.4657 (3)	1.0219 (2)	−0.12100 (15)	0.0630 (6)
C15	0.4359 (3)	0.9320 (2)	−0.12997 (14)	0.0630 (6)
C16	0.3279 (2)	0.89227 (14)	−0.08489 (13)	0.0539 (5)
C17	0.2611 (2)	0.71994 (13)	0.09812 (12)	0.0443 (5)
C18	0.2779 (2)	0.63601 (13)	0.14522 (11)	0.0436 (5)
C19	0.4050 (2)	0.6228 (2)	0.19261 (12)	0.0558 (6)
C20	0.4206 (3)	0.5450 (2)	0.23851 (13)	0.0679 (7)
C21	0.3113 (3)	0.4817 (2)	0.23689 (14)	0.0718 (7)
C22	0.1870 (3)	0.4938 (2)	0.19040 (14)	0.0686 (7)
C23	0.1689 (2)	0.57061 (14)	0.14481 (13)	0.0537 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1—C10	1.217 (2)	C4c—C8a	1.390 (3)
O2—C17	1.216 (2)	C8—C8a	1.381 (3)
N—C9	1.143 (3)	C8a—C8b	1.485 (3)
C1—C8c	1.388 (3)	C8b—C9	1.440 (3)
C4—C4A	1.378 (3)	C8b—C8c	1.515 (3)
C4a—C8e	1.401 (3)	C8b—C8d	1.599 (3)

C4a—C4b	1.523 (3)	C8c—C8d	1.512 (3)
C4b—C4c	1.520 (3)	C8c—C10	1.512 (3)
C4b—C8c	1.561 (3)	C8d—C8e	1.497 (3)
C4c—C5	1.386 (3)	C8d—C17	1.512 (3)
C4—C4a—C8e	120.7 (2)	C8d—C8c—C8b	63.79 (12)
C4—C4a—C4b	129.4 (2)	C10—C8c—C8b	123.2 (2)
C8e—C4a—C4b	109.7 (2)	C8d—C8c—C4b	104.61 (15)
C4c—C4b—C4a	105.1 (2)	C10—C8c—C4b	120.9 (2)
C4c—C4b—C8c	103.86 (15)	C8b—C8c—C4b	104.19 (15)
C4a—C4b—C8c	103.18 (15)	C8e—C8d—C8c	107.33 (15)
C5—C4c—C8a	120.1 (2)	C8e—C8d—C17	120.1 (2)
C5—C4c—C4b	129.6 (2)	C8c—C8d—C17	121.3 (2)
C8a—C4c—C4b	110.1 (2)	C8e—C8d—C8b	120.62 (15)
C8—C8a—C4c	121.2 (2)	C8c—C8d—C8b	58.19 (12)
C8—C8a—C8b	128.8 (2)	C17—C8d—C8b	114.08 (15)
C4c—C8a—C8b	109.9 (2)	C1—C8e—C4a	120.0 (2)
C9—C8b—C8a	118.1 (2)	C1—C8e—C8d	130.2 (2)
C9—C8b—C8c	123.9 (2)	C4a—C8e—C8d	109.4 (2)
C8a—C8b—C8c	107.8 (2)	N—C9—C8b	174.3 (2)
C9—C8b—C8d	115.1 (2)	O1—C10—C11	122.3 (2)
C8a—C8b—C8d	120.3 (2)	O1—C10—C8c	119.8 (2)
C8c—C8b—C8d	58.02 (12)	O2—C17—C18	122.2 (2)
C8d—C8c—C10	126.0 (2)	O2—C17—C8d	119.7 (2)

The structure was solved by direct methods. Full-matrix least-squares refinement was carried out by minimizing $w(F_o^2-F_c^2)^2$. The non-H atoms were refined anisotropically to convergence. H atoms were refined using an appropriate riding model.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

The authors thank the Council of Scientific and Industrial Research, Government of India (MM and MVG), NSF (CHE-9309690), Missouri Research Board, Center for Molecular Electronics and Department of Chemistry of the University of Missouri-St. Louis (NPR), and the Office of Basic Energy Sciences of the US Department of Energy (MVG, in part) for financial support of this work. This is document No. NDRL-3739 from the Radiation Laboratory and RRLT-PRU-52 from the Regional Research Laboratory, Trivandrum.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Asokan, C. V., Kumar, S. A., Das, S., Rath, N. P. & George, M. V. (1991). *J. Org. Chem.* **56**, 5890–5893.

Kumar, C. V., Murty, B. A. R. C., Lahiri, S., Chackacheri, E., Scaiano, J. C. & George, M. V. (1994). *J. Org. Chem.* **49**, 4923–4929.

Kumar, S. A., Asokan, C. V., Das, S., Wilbur, J. A., Rath, N. P. & George, M. V. (1993). *J. Photochem. Photobiol. A*, **71**, 27–31.

Murty, B. A. R. C., Pratapan, S., Kumar, C. V., Das, P. K. & George, M. V. (1995). *J. Org. Chem.* **50**, 2533–2538.

Pratapan, S., Ashok, K., Cyr, D. R., Das, P. K. & George, M. V. (1987). *J. Org. Chem.* **52**, 5512–5517.

Pratapan, S., Ashok, K., Gopidas, K. R., Rath, N. P., Das, P. K, & George, M. V. (1990). *J. Org. Chem.* **55**, 1304–1308.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1995). *SHELXTL-Plus*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). C**52**, 2802-2805

Bis(*o*-aminophénylammonium) Bis(*o*-phénylènediammonium) *cyclo*-Hexaphosphate Dihydrate

El Hassane Soumhi et Tahar Jouini

Département de Chimie, Faculté des Sciences, 1060 Campus Universitaire, Tunis, Tunisie. E-mail: jouini@stardent.cck.tn

(Reçu le 7 avril 1995, accepté le 15 mars 1996)

Abstract

The title compound, $2C_6H_9N_2^+.2C_6H_{10}N_2^{2+}.P_6O_{18}^{6-}.2H_2O$, contains $P_6O_{18}^{6-}$ anions connected by hydrogen bonds to water molecules and organic cations to form layers. The centrosymmetric P_6O_{18} groups are located around the inversion centres.

Commentaire

L'étude de l'intéraction de l'acide *cyclo*-hexaphosphorique et d'un cation organique peut être considérée comme récente. Elle a été initiée en 1989 par la caractérisation du premier *cyclo*-hexaphosphate organique, $[NH_3(CH_2)_2NH_3]_3P_6O_{18}.2H_2O$ (Durif & Averbuch-Pouchot, 1989). Depuis, quatre autres *cyclo*-hexaphosphates organiques ont été étudiés. Il s'agit de $(HONH_3)_6P_6O_{18}.4H_2O$ (Durif & Averbuch-Pouchot, 1990), des deux composés $(C_2H_5NH_3)_6P_6O_{18}.4H_2O$ et $(N_2H_5)_2(N_2H_6)_2P_6O_{18}$ (Averbuch-Pouchot & Durif, 1991*a*) et plus récemment de $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]_2P_6O_{18}.2H_2O$ (Gharbi, Jouini & Durif, 1995). Ces composés, tous à cations organiques aliphatiques, ont été préparés selon la méthode de Boullé (1938), sauf le dernier, par échange d'ions sur résine.

La structure renferme des couches organiques et inorganiques alternées. Les deux groupements organiques de l'unité asymétrique pointent dans la même direction et se connectent, par liaisons hydrogène de type N—H···O—P, à la couche inorganique vers laquelle ils sont orientés. Il en résulte que les anions $P_6O_{18}^{6-}$ et les cations organiques qui leur sont liés forment des couches imbriquées, parallèles au plan *ac*. Chaque molécule d'eau est liée à deux anions $P_6O_{18}^{6-}$ et à un groupement organique.