

Table 1. Selected geometric parameters (Å, °)

C3—O1	1.460 (5)	C14—C27	1.556 (6)
C4—C23	1.541 (6)	C15—C16	1.322 (6)
C4—C24	1.563 (6)	C20—C30	1.520 (7)
C8—C26	1.538 (5)	C20—C29	1.529 (6)
C8—C14	1.595 (6)	C31—O2	1.194 (6)
C10—C25	1.544 (6)	C33—O4	1.212 (8)
C13—C18	1.331 (5)		
C2—C3—C4	114.2 (4)	C16—C15—C14	123.6 (5)
C26—C8—C14	106.7 (3)	C15—C16—C17	124.9 (4)
C18—C13—C14	123.7 (4)	C13—C18—C17	123.2 (4)
C27—C14—C8	112.7 (3)		
C1—C2—C3—O1	177.5 (3)	C14—C15—C16—C17	3.6 (7)
O1—C3—C4—C5	-174.5 (3)	C12—C13—C18—C19	-2.5 (6)
C26—C8—C14—C27	175.3 (4)	C32—C31—O1—C3	178.1 (5)

Table 2. Ring-puckering parameters (Å, °) for four rings

Ring	q ₂	q ₃	Q _T	θ
A	0.019 (5)	0.551 (4)	0.551 (4)	2.0 (5)
B	0.089 (4)	0.565 (5)	0.572 (5)	8.9 (4)
C	0.067 (5)	0.572 (4)	0.576 (4)	6.7 (5)
E	0.049 (5)	0.572 (5)	0.574 (5)	4.9 (5)

One of the C atoms (C34) was found to be affected by disorder: this was modelled in terms of two equally occupied sites following refinement of the occupancies to 0.55 (5) and 0.45 (5). The distances between these isotropic components and C33 were restrained to 1.52 (1) Å. All other non-H atoms were refined with anisotropic displacement parameters. All H atoms were included at geometrically calculated positions, except for those of methyl groups attached to sp² centres (i.e. for C32, C34A and C34B), where the H atoms were located from a circular difference Fourier synthesis. In the refinement, the idealized methyl groups centred on C32, C34A and C34B were allowed to rotate about the local C—C vector, while other H atoms were then allowed to ride on their parent atoms. Hydrogen displacement parameters were also allowed to ride, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl H atoms and $x = 1.2$ for all others.

As the absolute structure could not be determined reliably from the Flack parameter [0.2 (5)] and there are no comparable structures where the absolute structure is known, the enantiomer shown cannot be regarded as having been satisfactorily established.

Data collection: local program (Belletti *et al.*, 1993). Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ZORTEP (Zsolnai & Huttner, 1994). Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1304). Services for accessing these data are described at the back of the journal.

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Uronium sulfate, [OHC(NH₂)₂]₂(SO₄)

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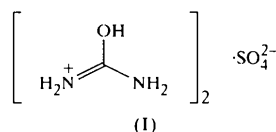
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Abstract

The title compound crystallizes in the orthorhombic space group *Pbca*. In the crystal structure, the two H atoms of sulfuric acid protonate the carbonyl groups of two urea molecules. The H—O(urea) distances are 0.83 (3) and 0.87 (2) Å, with O(urea)—O(sulfate) distances of 2.544 (2) and 2.571 (2) Å, respectively.

Comment

The existence of the title compound, uronium sulfate, was deduced, based on a phase-diagram study, about 63 years ago (Dalman, 1934). However, the synthesis of this compound has never been reported; neither crystals nor crystal structure data have been available up to the present. In recent years, we have found that this compound has the important property of activating the phosphorus from phosphatic rock and soil. Uronium sulfate has therefore been applied widely in the manufacture of phosphatic and compound fertilizers (Chen & Xiao, 1989). We report here the synthesis and crystal structure of the title compound, (I). The



crystal structure of (I) is shown in Fig. 1, and is qualitatively similar to that seen for uronium nitrate by X-ray (Harkema & Feil, 1969) and neutron (Worsham & Busing, 1969) diffraction. The atomic arrangement on the a - c plane is shown in Fig. 2. In a subsequent article, we will give a detailed analysis of the bond structure and electronic density of states, obtained by embedded-cluster density-functional methodology, and comment on its consequences for phosphorus activation.

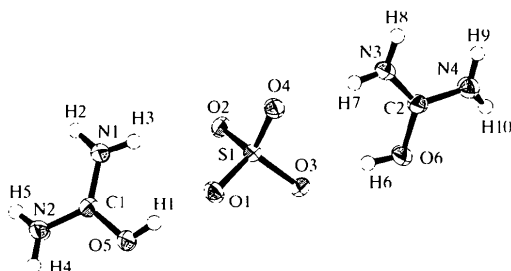


Fig. 1. The crystal structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

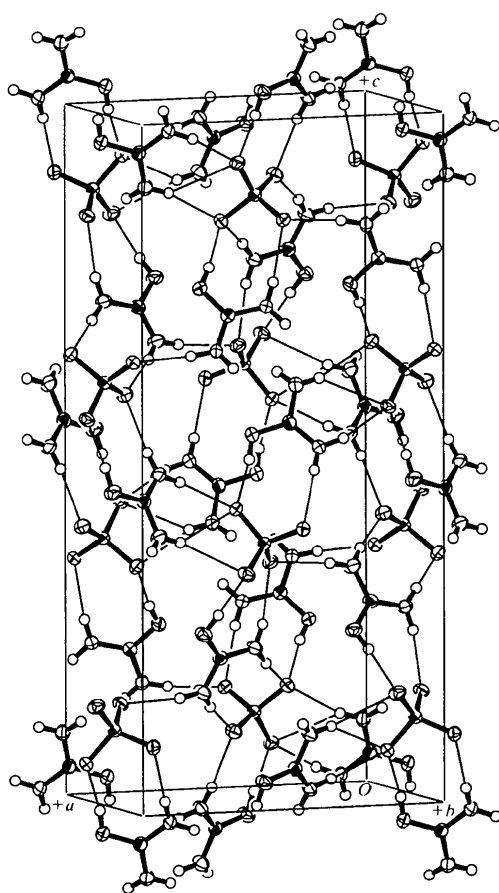
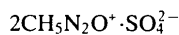


Fig. 2. Atomic arrangement on the a - c plane.

Experimental

The title compound was synthesized from the reaction of urea and sulfuric acid. To a 25 ml round-bottomed flask under nitrogen, 96.0% sulfuric acid (5.10 g, 0.05 mol) was added, followed slowly by ground ultra-pure urea (6.00 g, 0.10 mol) with stirring. After the solid had dissolved, the solution was allowed to stand at 293 K overnight.

Crystal data



$$M_r = 218.18$$

Orthorhombic

Pbca

$$a = 10.594(2) \text{ \AA}$$

$$b = 7.461(4) \text{ \AA}$$

$$c = 22.920(5) \text{ \AA}$$

$$V = 1811.6(9) \text{ \AA}^3$$

$$Z = 8$$

$$D_x = 1.600 \text{ Mg m}^{-3}$$

D_m not measured

Mo $K\alpha$ radiation

$$\lambda = 0.7107 \text{ \AA}$$

Cell parameters from 25

reflections

$$\theta = 12.0\text{--}13.0^\circ$$

$$\mu = 0.368 \text{ mm}^{-1}$$

$$T = 153.2 \text{ K}$$

Columnar

$$0.77 \times 0.43 \times 0.26 \text{ mm}$$

Colorless

Data collection

CAD-4 diffractometer

ω - θ scans

Absorption correction:

analytical (de Meulenaer
& Tompa, 1965)

$$T_{\min} = 0.855, T_{\max} = 0.909$$

2188 measured reflections

2078 independent reflections

1404 reflections with

$$I > 3\sigma(I)$$

$$R_{\text{int}} = 0.012$$

$$\theta_{\max} = 25.97^\circ$$

$$h = -13 \rightarrow 2$$

$$k = -1 \rightarrow 9$$

$$l = -28 \rightarrow 5$$

3 standard reflections

every 90 reflections

intensity decay: -0.4%

Refinement

Refinement on F^2

$$R(F) = 0.023$$

$$wR(F^2) = 0.034$$

$$S = 2.440$$

1404 reflections

159 parameters

All H atoms refined

isotropically

$$w = 1/[\sigma^2(F_o) + 0.00002|F_o|^2]$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.19 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\min} = -0.33 \text{ e \AA}^{-3}$$

Extinction correction:

Zachariasen (1967)

Extinction coefficient:

$$7.7(4) \times 10^{-7}$$

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Hydrogen-bonding geometry (\AA , $^\circ$)

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O5—H1...O1	0.87 (2)	1.70 (2)	2.571 (2)	171 (2)
O6—H6...O3	0.83 (3)	1.73 (3)	2.544 (2)	168 (3)
N1—H3...O2	0.84 (3)	2.06 (3)	2.893 (2)	169 (2)
N2—H4...O2 ⁱ	0.88 (2)	2.07 (2)	2.915 (2)	163 (2)
N2—H5...O4 ⁱⁱ	0.81 (2)	2.04 (2)	2.843 (2)	169 (2)
N3—H7...O4	0.88 (2)	2.00 (2)	2.870 (2)	173 (2)
N3—H8...O3 ⁱⁱⁱ	0.87 (2)	2.07 (2)	2.882 (2)	154 (2)
N4—H10...O2 ^{iv}	0.81 (2)	2.13 (2)	2.916 (3)	164 (2)

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

The structure was solved by direct methods and expanded using Fourier techniques (Altomare *et al.*, 1993). The non-H atoms were refined anisotropically. All calculations were per-

formed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1997).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1397). Services for accessing these data are described at the back of the journal.

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Regioselectivity in dibenzobarrelene photorearrangements: photoproducts derived from 9-substituted-dibenzobarrelenes

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Abstract

Irradiation of the 9-formyl-, 9-acetyl-, 9-nitro- and 9-*tert*-substituted dibenzobarrelenes gave the corresponding 4b-substituted dibenzosemibullvalenes, (2a) (8b, 8c-dibenzoyl-4b, 8b, 8c, 8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene-4b-carbaldehyde, C₃₁H₂₀O₃), (2b) (4b-acetyl-8b, 8c-dibenzoyl-4b, 8b, 8c, 8d-tetra-

hydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene, C₃₂H₂₂O₃), (2c) (8b, 8c-dibenzoyl-4b-nitro-4b, 8b, 8c, 8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene, C₃₀H₁₉NO₄) and (2d) (8b, 8c-dibenzoyl-4b-*tert*-butyl-4b, 8b, 8c, 8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene). The product (2d) gave the corresponding dibenzopentalenofuran derivative, (3d) (10c-benzoyl-6b-*tert*-butyl-2-phenyl-10b, 10c-dihydro-6b-*H*-dibenzo[*a,f*]furo[2,3,4-*cd*]pentalene, C₃₄H₂₈O₂). The structures of (2a), (2b), (2c) and (3d) have been established unequivocally *via* X-ray crystallographic analysis. The molecular structures of (2a), (2b), and (2c) incorporate the basic dibenzosemibullvalene skeleton, which contains the 6:5:5:6:3 fused ring system with normal bond lengths and bond angles. The crystal structures of (2a), (2b), and (2c) have intermolecular hydrogen-bonding interactions (< 2.60 Å) which are almost linear around the H atoms. The structure of (3d) shows a 6:5:5:6:5 fused ring system and does not indicate hydrogen-bonding-type intermolecular interactions.

Comment

Several aspects of the photorearrangement of dibenzobarrelenes containing the 1,2-dibenzoylalkene moiety are reported in the literature (Kumar *et al.*, 1984, 1993, 1996, 1997; Murty *et al.*, 1985; Pratapan *et al.*, 1987, 1990; Asokan *et al.*, 1991; Scheffer & Yang, 1995; Mathew *et al.*, 1996a,b; Ramaiah *et al.*, 1996; Muneer *et al.*, 1996). It has been found that the observed regioselectivity in these rearrangements depends on several factors, including the electronic and steric requirements of the bridgehead substituents. Thus, it has been observed that if an electron-withdrawing substituent such as the cyano group is present at the bridgehead position of the starting dibenzobarrelene, then the 8b-cyanosubstituted dibenzosemibullvalene is formed on irradiation (Murty *et al.*, 1985; Muneer *et al.*, 1996). On the other hand, the presence of substituents such as methyl, methoxy, formyl, acetoxy *etc.* at the bridgehead position of the starting dibenzobarrelenes results in the formation of the corresponding 4b-substituted dibenzosemibullvalenes upon irradiation (Murty *et al.*, 1985). In view of the importance of understanding the role of bridgehead substituents in the observed regioselectivity in the photorearrangements of dibenzobarrelenes, it became essential to determine the structures of the photoproducts unambiguously through X-ray crystallographic analysis.

In the present study, we have examined the structures of the photoproducts (2a), (2b), (2c) and (3d), derived from the dibenzobarrelenes, 11,12-dibenzoyl-9,10-dihydro-9-formyl-9,10-ethenoanthracene (1a), 9-acetyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (1b), 11,12-dibenzoyl-9,10-dihydro-9-nitro-9,10-ethenoanthracene (1c) and 9-*tert*-butyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (1d), respectively. It has been reported earlier, on the basis