

(quartet) and 1.02 ppm (triplet); $T = -80^\circ$, δ (NMe) 4.28 (singlet), δ (NCH₂CH₃) 2.38 (quartet) and 0.95 ppm (triplet). Cf. W₂(NEt₂)₆, $T = +75^\circ$, 3.65 (quartet), 1.11 ppm (triplet); $T = -60^\circ$, 4.87 and 2.37 ppm (quartets) and 1.30 and 0.97 ppm (triplets). δ in parts per million relative to Me₆Si₂O.

- (6) R. E. McCarley, private communication.
 (7) Calcd (found) for: W₂(NMe₂)₆, C, 22.81 (22.74); H, 5.70 (5.60); N, 13.30 (13.17). W₂(NMeEt)₆, C, 30.18 (30.21); H, 6.75 (6.60); N, 11.73 (11.61). W₂(NEt₂)₆, C, 36.01 (36.13); H, 7.56 (7.60); N, 10.50 (10.37).
 (8) Analysis for W(NEt₂)₂Cl calcd (found): C, 26.43 (26.52); H, 5.55 (5.57); N, 7.71 (7.60); Cl, 9.75 (9.41). W₂(NEt₂)₄Cl₂ reacts with 2LINEt₂ to give W₂(NEt₂)₆.
 (9) D. C. Bradley, C. W. Newling, and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 411 (1971).
 (10) These compounds are, however, considerably less thermally stable than analogous Mo₂(OR)₆ compounds (ref 4) and substantial decomposition accompanies sublimation.
 (11) M. H. Chisholm and M. Extine, *J. Am. Chem. Soc.*, **97**, 1625 (1975); **96**, 6214 (1974).
 (12) Similar CO₂ exchange has been noted for other early transition metal *N,N*-dialkylcarbamates: M. H. Chisholm and M. Extine, *J. Chem. Soc., Chem. Commun.*, 438 (1975).
 (13) P. C. H. Mitchell and R. D. Scarle, *J. Chem. Soc., Dalton Trans.*, 110 (1975).
 (14) F. A. Cotton, Chemical Society Centenary Lecture, 1974; *Chem. Soc. Rev.*, **14**, 27 (1975).
 (15) For example, compare Cr(NEt₂)₃ which is dimeric and paramagnetic in solution: D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, **15**, 259 (1972).

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Electron Density Distribution in Cumulenes. A Low Temperature X-Ray Study of Tetraphenylbutatriene

Sir:

In recent years accurate X-ray (and neutron) diffraction measurements at low temperatures, together with the development of various computational techniques,¹ have led to significant progress in determining the electron density distribution in a chemical bond.

As part of a study on the correlation between the alignment of π electrons in crystalline ethylenes and their photo-reactivity² we have mapped the bonding densities in a butatriene³ chain confirming that the π densities of adjacent C=C bonds lie in mutually perpendicular planes. The molecular difference density was derived from low temperature X-ray data with the aid of a charge deformation model as developed by Hirshfeld.^{1b} In this method, the charge displacement is expanded in a basis of localized deformation functions centered on the several atoms, and the coefficients of these functions are determined by least squares from the X-ray intensities.

X-Ray diffraction data of tetraphenylbutatriene⁴ were collected at $\sim 100^\circ\text{K}$ on a computer-controlled Nonius CAD-3 diffractometer⁵ with graphite-monochromatized Mo $K\alpha$ radiation. A total of 22241 reflections were measured up to $\theta = 40^\circ$, yielding 8325 independent reflections. The structure was refined by full-matrix least-squares adjustment of 341 parameters; these included 92 electron-density deformation coefficients, 144 positional, and 104 thermal parameters. A thermal-motion rigid-body constraint⁶ was applied to each of the phenyl rings.

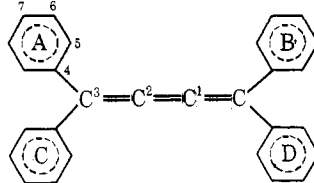
Final reliability indices were $R = 0.07$ and

$$r = [\Sigma w(F_o^2 - K^2 F_c^2)^2 / \Sigma w F_o^4]^{1/2} = 0.08$$

The quality of the structure determination⁷ is reflected in the low estimated variances of the mean bond lengths of chemical equivalent bonds shown in Table I.

The deformation densities showed accumulation of charge between bonded atoms, with the carbon atoms lying

Table I. Mean Bond Lengths (Å), Their Estimated Variances^a and Their Estimated Net "Bonding" Charge (electrons)



Bonds	Mean bond length	Net charge
C ₁ -C ₂	1.2596	0.30
C ₂ -C ₃	1.3479 (6)	0.22
C ₃ -C ₄	1.4775 (5)	0.11
C ₄ -C ₅	1.4063 (10)	0.20
C ₅ -C ₆	1.3936 (8)	0.20
C ₆ -C ₇	1.3986 (15)	0.20

^a $\sigma^2(\bar{l}) = \Sigma(l_i - \bar{l})^2/n(n-1)$, where \bar{l} is the mean and n is the number of chemically equivalent bonds.

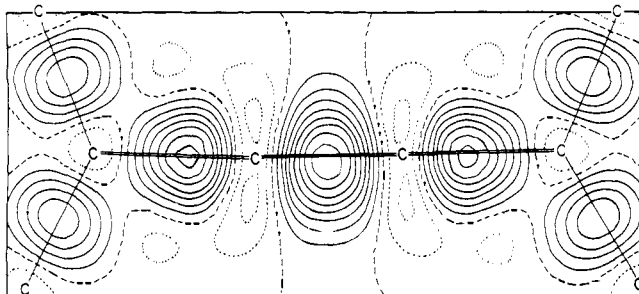


Figure 1. Deformation density in the butatriene plane ($>C=C=C<$). Contour interval $0.1 \text{ e}/\text{\AA}^3$; zero contour broken, negative contours dotted.

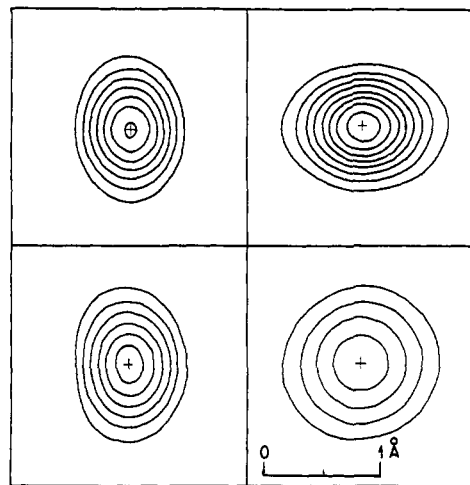


Figure 2. Deformation density sections perpendicular to the various C-C bonds through their centers: (top left, a) the outer C²=C³ bond, (top right, b) the inner C¹=C² bond, (bottom left, c) an aromatic bond, (bottom right, d) the exocyclic C³-C⁴ bond. The vertical direction is perpendicular to the butatriene plane for (a) and (b) and to the phenyl plane for (c) and (d). Contours as in Figure 1. The center of the bond is marked +.

in shallow troughs of negative difference density. In the butatriene chain the peak heights at the bond centers (Figure 1) are $0.9 (\pm 0.05)$ and $0.75 (\pm 0.05) \text{ e}/\text{\AA}^3$ for the inner and outer C=C bonds. The density sections perpendicular to these two bonds through their centers (Figure 2a, b) are elliptic, with their long axes mutually perpendicular, the charge in the outer C=C bond is elongated along the normal to the butatriene plane while that in the inner C=C bond is elongated in the plane.

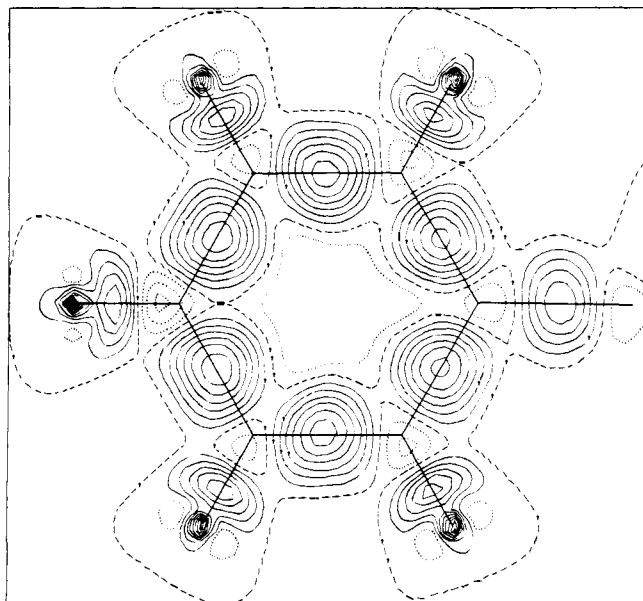


Figure 3. Deformation density section through the plane of the phenyl ring. Contours are as in Figure 1.

These charge distributions are in agreement with classical theory of π electrons in cumulenic systems.

The bonding density distribution in the phenyl plane is shown in Figure 3. The density sections through the aromatic bonds (Figure 2c) show the π character above (and below) the phenyl plane, whereas the electron distribution in the exocyclic C-C bond (Figure 2d) appears to be purely σ .

The net charge⁸ in each of the several C-C bonds (Table I) is related to the bond length, varying between 0.1 and 0.3 electrons for bonds between 1.48 and 1.26 Å.

The electron density peak in the inner bond appears to be more circular in shape than that in the outer bond, suggesting a measure of out-of-plane π density in this bond. Moreover, this inner C=C bond is decidedly shorter (1.260 vs. 1.348 Å) and contains more electrons (0.3 vs. 0.22 e) than the outer C=C bond implying some C=C triple bond character.

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References and Notes

- (1) P. Coppens and A. Vos, *Acta Crystallogr., Sect. B*, **27**, 146 (1971); (b) M. Harel and F. L. Hirshfeld, *ibid.*, **31**, 162 (1975), and references therein.
- (2) Z. Berkovitch-Yellin, M. Lahav, and L. Leiserowitz, *J. Am. Chem. Soc.*, **96**, 918 (1974).
- (3) Similar investigations are presently being carried out on the allene system (in the 1:1 complex allenedicarboxylic acid, acetamide), together with Nader. These works are part of a joint study of cumulenes, carried out by us and by F. Nader and H. Irngartinger, Chemistry Department, University of Heidelberg.
- (4) The cell constants (100°K) are: $a = 10.035$ (3), $b = 10.458$ (4), $c = 9.978$ (3) Å; $\alpha = 105.04$ (4), $\beta = 105.27$ (3), $\gamma = 92.17$ (3)°. Space group $P1$, $Z = 2$.
- (5) F. Van Bolhuis, *J. Appl. Crystallogr.*, **4**, 263 (1971).
- (6) V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 63 (1968).
- (7) The molecule is nonplanar, the phenyl rings A,B,C,D make dihedral angles of 30, 28, 39, and 42°, respectively, with the plane through the butatriene system $>C=C=C=C<$ (see structure in Table I). The butatriene chain is almost linear, the C=C=C angles being 176.2°.
- (8) The net charge in each bond was computed by numerical integration.

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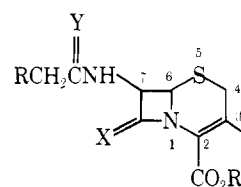
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β -Thionolactam Analogs of Cephalosporins and Penicillins

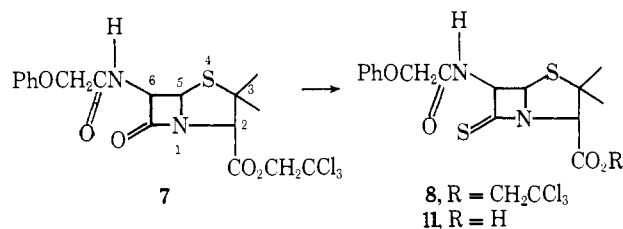
Sir:

In recent years an increasing number of nuclear modified β -lactam antibiotics have been described, in some instances with retention¹ or enhancement² of antibacterial activity. Excepting 7 (6)³ and 2⁴ (2)⁵ substituted cephalosporins (penicillins), these modifications are remote from the 1-8 (1-7) bond, the rupture of which is an essential step in the mechanism of action of β -lactam antibiotics. To determine the effect of substitution adjacent to this bond, we set out to prepare the β -thionolactam counterparts of β -lactam antibiotics.

Phosphorus pentasulfide is reported⁶ to react preferentially with the side-chain amide of trichloroethyl ester **1**. The product (**2**) of this reaction was converted, via hydrolysis of an intermediate iminothioether, to the free 7 β -amine. This conversion establishes the position of sulfur in **2** unambiguously. Boron sulfide is more reactive than phosphorus pentasulfide in carbonyl-thiocarbonyl transformations.⁷ This communication describes the utility of boron sulfide for preparation of β -thionolactam analogs of cephalosporins and penicillins.



No.	R	Y	X	R'
1	PhO	O	O	CH ₂ CCl ₃
2	PhO	S	O	CH ₂ CCl ₃
3	PhO	O	S	CH ₂ CCl ₃
4	PhO	S	S	CH ₂ CCl ₃
5	Ph	O	O	CH ₂ CCl ₃
6	Ph	O	S	CH ₂ CCl ₃
9	PhO	O	S	H
10	Ph	O	S	H



Reaction of **1** with 2 equiv of boron sulfide in refluxing chloroform overnight gave two major products and unreacted **1**. Chromatography on silica gel gave the β -thionolactams **3** and **4** in 20 and 10% yields, respectively; preparative TLC gave analytically pure **3** (C, H, N, Cl, S)⁸ and **4** (C, H, N, Cl, S)⁸ as foams. The absence of the characteristic " β -lactam" band at 1780 cm^{-1} and the appearance of a new intense band at 1400 cm^{-1} in their infrared spectra distinguished **3** and **4** from their β -lactam precursor **1**.⁹ All of the β -thionolactams prepared exhibited a band in the region of 1370-1420 cm^{-1} attributable to the β -thionolactam moiety. The ultraviolet spectra of **3** and **4** exhibit intense maxima at 313 nm.

The chemical shift data in Table I are in accord with the assignment of side-chain thionamide in **2** and β -thionolactam in **3**; in particular, the downfield shift of the side-chain methylene protons of **2** and **4** and the opposite shifts of H₆ and H₇ in **3** are noted. A comparison of the mass spectra of **1-4** confirms these assignments. Observation of the appro-