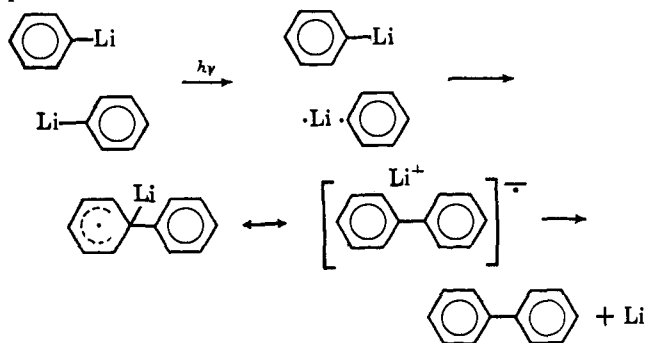cation. As the biphenyl radical anion is unstable in ether, lithium metal and biphenyl result.[10] The postulated reaction sequence is

Alternatively, *direct* formation of biphenyl, or synchronous generation and coupling of two phenyl radicals, from the dimer would account for these results.

(10) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, 58, 2442 (1936).

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Structure of the Complex $CaBr_2 \cdot 10H_2O \cdot 2(CH_2)_6N_4$

Sir:

A long time ago Barbieri and Calzolari[1] described a class of crystalline complexes having the general formula $MeX_2 \cdot nH_2O \cdot 2HMT$, where $Me = Ca^{2+}$, Ni^{2+}, Mg^{2+}, Co^{2+}, Ba^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Sr^{2+}; $X = Cl^-$, Br^-, I^-, SCN^-, NO_2^-, NO_3^-, ClO_4^-, $S_2O_3^{2-}$, SO_4^{2-}, $S_2O_6^{2-}$, $Cr_2O_7^{2-}$; HMT is hexamethylenetetramine. The most frequent value of n is 10 and a large group of complexes with ten water molecules appears to be isomorphous from a crystallographic examination. The formation of these complexes through crystallization from water solutions has been ascribed[1] to the tendency of HMT to stabilize high hydration forms of the inorganic salts.

In our laboratory a three-dimensional study of $CaBr_2 \cdot 10H_2O \cdot 2HMT$ was carried out in order to establish the general features of the structure of this class of complexes. This compound was already investigated by a two-dimensional X-ray analysis by Bertinotti and Liquori,[2] but unfortunately the many superpositions of atoms in the projections did not allow a detailed solution of the crystal structure. The crystals were grown as platelets from a solution containing $CaBr_2$ and HMT in the proper stoichiometric ratio. The unit cell is triclinic and the parameters are: $a = 9.89$, $b = 9.75$, $c = 9.58$ Å.; $\alpha = 94° 29'$, $\beta = 100° 39'$, $\gamma = 119° 20'$; $d_{calcd} = 1.41$ g./cm.^{3}; $V = 776$ Å.^{3}; $n = 1$.

Since the chemical formula of the complex is fully consistent with a centrosymmetric distribution of the

(1) G. A. Barbieri and F. Calzolari, *Atti Accad. Nazl. Lincei, Rend.' Classe Sci. Fis. Mat. Nat.*, [2] 19, 584 (1910); [1] 20, 119 (1911).
(2) F. Bertinotti and A. M. Liquori, *Ric. Sci.*, 23, 1823 (1953).
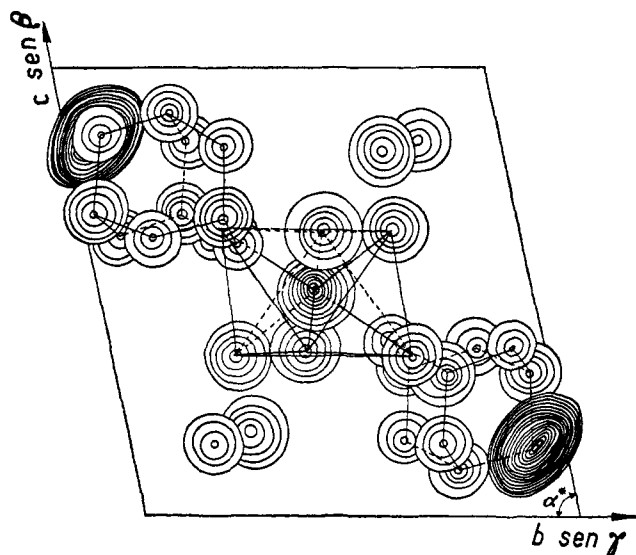

Figure 1. Composite projection of the three-dimensional electron density distribution on (100). Contours are at intervals of 4 electrons Å.$^{-3}$ around the calcium and bromide ions and at intervals of 2 electrons Å.$^{-3}$ around the other atoms, starting from 2 electrons Å.$^{-3}$.

atoms in the unit cell, the space group $P_{\bar{1}}$ was assumed. The density measured in a density gradient was found to be 1.44 g./cm.^{3}, slightly higher than the calculated value, probably because of the tendency of the crystals to transform into the cubic modification investigated by Addamiano and Giacomello.[3] Seventeen self-correlating levels were collected with the use of a Weissenberg camera and Cu $K\alpha$ radiation on a crystal mounted on the (100) and (010) axes. After the usual corrections, the intensities were scaled together using the method of Rollet and Sparks.[4]

The phase problem was solved taking advantage of the high scattering power of the Ca^{2+} and Br^- ions. The calcium was placed, from space group considerations, at the center of symmetry, and the coordinates of the bromine atom were derived from a three-dimensional Patterson function. After two cycles of three-dimensional Fourier and structure factor calculations, a value of $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.19$ was obtained. Isotropic thermal corrections for individual atoms were calculated from the electron density peaks of the three-dimensional Fourier synthesis.[5,6] Further refinement is contemplated considering the anisotropic rigid body oscillations of the HMT molecules.

The three-dimensional electron density distribution shows up very clearly the structure of the complex as may be observed from the composite drawn in Figure 1 on (100). A schematic representation of the crystal structure is shown in Figure 2.

As was already foreseen from the study in projection,[2] the Ca^{2+} octahedrally coordinates six molecules of water at a distance of 2.3 Å. The threefold axis of the HMT is oriented approximately along the c axis. Three of the nitrogen atoms of each HMT molecule are linked by hydrogen bonds N···H···O to the octahedrally coordinated water molecules surrounding three different calcium ions. This results in a two-

(3) A. Addamiano and G. Giacomello, *ibid.*, 21, 2121 (1951).
(4) J. S. Rollet and R. A. Sparks, *Acta Cryst.*, 13, 273 (1960).
(5) F. Bertinotti and A. M. Liquori, *Ric. Sci.*, 26, 2118 (1956).
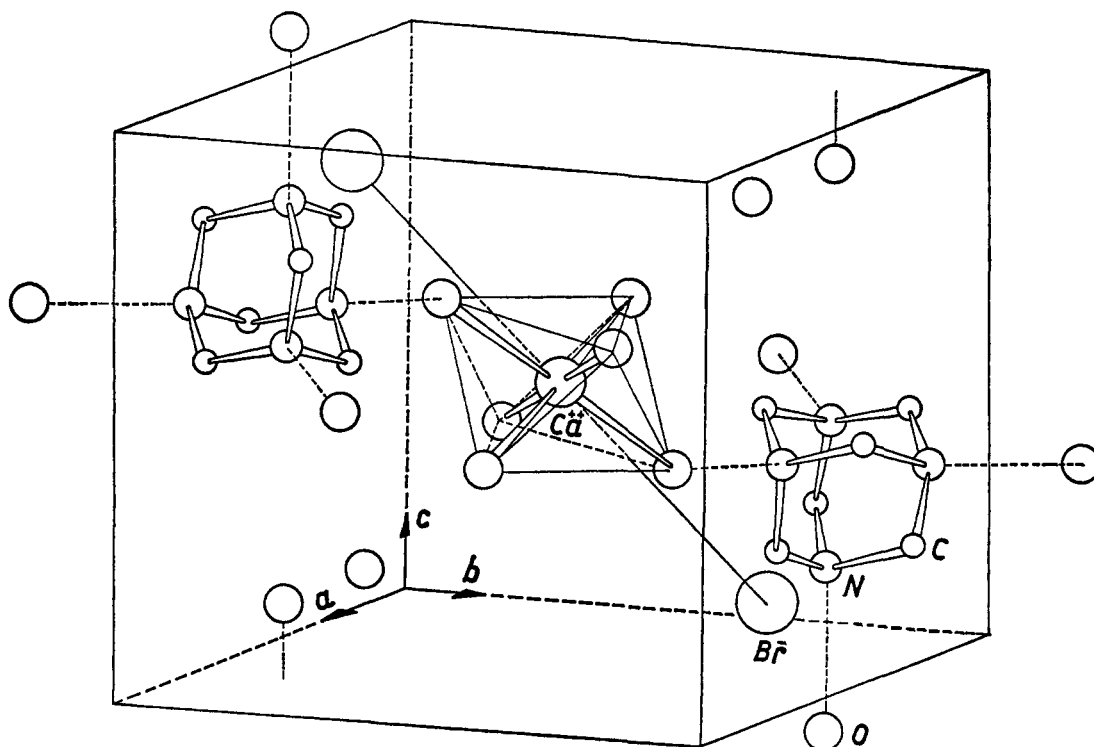(6) A. Damiani, E. Giglio, and A. Ripamonti, *Ric. Sci., Rend. Sez. A*, [7] 3, 757 (1963).

Figure 2. View of the crystal structure: $Ca^{2+}-O = 2.3$ Å.; $Br^--Ca^{2+} = 5.2$ Å.; N-H-O (broken line) = 2.8 Å.; $(C-N)_{av} = 1.47$ Å.; $\angle(C-N-C)_{av} = 108°$; $\angle(N-C-N)_{av} = 112°$.

dimensional network in the (001) plane. These layers are linked together only by chains of hydrogen bonds between water and HMT nitrogen atoms and van der Waals interactions. The Br^- ions are at 5.2 Å. from the Ca^{2+} ion, which appears to be the distance of closest approach, taking into account the screening effect of the water molecules surrounding the central cation and the van der Waals interactions between the Br^- and HMT molecules. It is gratifying that all bond angles and bond lengths in the HMT are in good agreement with the values found in the structure of HMT recently refined by Cruickshank.[7]

Acknowledgment. We wish to thank Dr. E. Benedetti and Dr. G. Elefante for their collaboration and Professor V. Caglioti for initially suggesting this problem.

(7) L. N. Becka and D. W. J. Cruickshank, *Proc. Roy. Soc.* (London), 273, 435 (1963).

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Benzene- and Toluene-Photosensitized Isomerization of 1,2-Dimethylcyclopropane. The Triplet State of Cyclopropane
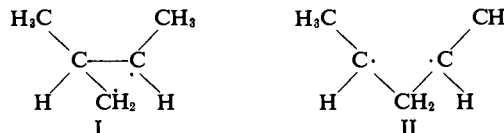
Sir:

We wish to report the initial results of a study undertaken to shed more light on the mechanism of triplet methylene addition to olefins. Previous work has shown that *cis-* or *trans*-1,2-dimethylcyclopropane activated thermally[1] or "chemically"[2-6] yields *trans-*

(1) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.* (London), A257, 122 (1960); A260, 424 (1961).
(2) H. M. Frey, *ibid.*, A251, 575 (1959).

or *cis*-1,2-dimethylcyclopropane, *cis-* and *trans*-pentene-2, 2-methylbutene-1, and 2-methylbutene-2 as products. The reaction of triplet methylene with butene-2[4-9] yields the foregoing products and, in addition, 3-methylbutene-1.

A mechanism suggested for the triplet methylene reaction[9] involves the initial formation of a triplet addition complex (biradical I). Since the relative

$$\begin{array}{cc} & \\ H_3C \quad CH_3 & H_3C \quad CH_3 \\ \diagdown \diagup & \diagdown \diagup \\ C——C & C\cdot \quad \cdot C \\ \diagup \quad \diagdown & \diagup \quad \diagdown \\ H \quad CH_2 \quad H & H \quad CH_2 \quad H \\ I & II \end{array}$$

yields of products in this reaction do not, however, appear to be consistent with this mechanism, another mechanism has been proposed[10] which involves the initial formation of triplet 1,2-dimethylcyclopropane. This species may be visualized as a resonance hybrid of valence bond structures like I and II and readily explains the observed product yields.

This latter mechanism requires that the exothermicity of the triplet methylene–butene-2 reaction be greater than or equal to the unknown triplet state energy of 1,2-dimethylcyclopropane. Since the heats of formation of butene-2 and 1,2-dimethylcyclopropane are probably nearly the same (by analogy with other olefins and

(3) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, 40, 1425 (1962).
(4) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, 68, 1322 (1964).
(5) S. Ho, I. Unger, and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, 87, 2297 (1965).
(6) R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, 43, 1631 (1965).
(7) F. A. L. Anet, R. F. W. Bader, and A. M. Van der Auwera, *J. Am. Chem. Soc.*, 82, 3217 (1960).
(8) H. M. Frey, *ibid.*, 82, 5947 (1960).
(9) H. M. Frey, *ibid.*, 82, 5947 (1960).
(9) F. J. Duncan and R. J. Cvetanović, *ibid.*, 84, 3593 (1962).
(10) J. A. Bell, *Progr. Phys. Org. Chem.*, 2, 45 (1964); in ref. 6 this same idea is advanced.