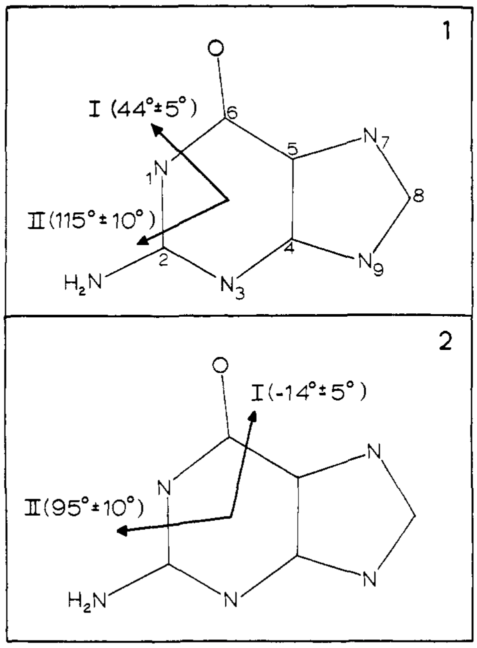

Figure 2. The two possible assignments of transition moment directions in 9-ethylguanine as deduced from combined information from polarized specular reflectance measurements on single crystals and from fluorescence polarization. I denotes the 270-nm band and II the 253-nm band. The ambiguity may be resolved by measurements on crystals of other guanine derivatives.

strongly as I (II is about half again as intense as I) is due to the fact that N_2–C_8 is perpendicular to the *ac* face in half the molecules. There is also evident in the *a*-polarized spectrum a small dip at 35.5 kK, presumably due to a component of I. Thus, the transition moment of I is not directed exactly perpendicular to N_2–C_8, although it is predominantly so. This leaves a twofold ambiguity for the direction of I.

One may summarize qualitative deductions at this point by saying that II is polarized close to the N_2–C_8 direction while I is either polarized nearly short axis or else close to the N_1–N_3 direction.

Using an inductive method in a manner previously described,[4] in which an oriented-gas model is assumed and the experimental curves are fitted approximately using a three-term Sellmeier formula, one finds, more quantitatively, that I makes an angle of 61 ± 5° with N_2–C_8 while II may lie anywhere within 20° of N_2–C_8. (The rather large limit is mainly due to the closeness in energy of the two transitions. Small inflections in the reflection curve due to II could be masked by the effects of I.)

When the directions are defined according to the Devoe–Tinoco convention[5] as the angle with the N_3–C_6 direction (and such that N_2–C_8 is 105°), the direction of I is either 44 ± 5 or −14 ± 5° and the direction of II is between 85 and 125°.

The result is in agreement with the previous fluorescence polarization observations[3a] which indicated that the two transitions have approximately perpendicular moments. Quantitative assessment of the fluorescence data using an analysis similar to that of Albrecht[6] leads to the conclusion that it is highly unlikely that the angle between the transition moments is less than 65°. To the extent that intermolecular interactions in the crystal do not significantly alter dichroic ratios relative to the corresponding oriented gas, this information may be coupled with the specular reflectance result to narrow the possibilities somewhat. The two possibilities are: (1) I is 44 ± 5° and II is 115 ± 10° or (2) I is −14 ± 5° and II is 95 ± 10°. These results are summarized in Figure 2. Recent specular reflectance measurements of Clark and coworkers[7] on single crystals of guanine hydrochloride should remove the ambiguity, assuming that protonation does not significantly affect the transition moment directions.

Having measured transition moment directions in the DNA bases makes it possible to assess the adequacy of the large number of quantum mechanical calculations of electronic structure which have been carried out for these molecules (see ref 4).

There have been eight molecular orbital treatments of the π electrons of guanine in which the transition moment directions for the first two transitions have been calculated. The calculations range in sophistication from simple Hückel to approximate SCF with configuration interaction. The results are quite similar for all the calculations, ranging from 104 to 135° for the 270-nm band and from 14 to 45° for the 253-nm band.

It is seen that these results are not in accord with the experimental results presented here. A possibility is that these methods reverse the order of the first two states. Application[8] of the interlocking amide resonance theory of Rosa and Simpson,[9] on the other hand, appears to give the correct order, predicting 35 and 130° for the 270- and 253-nm transitions, respectively.

Acknowledgment. We wish to acknowledge Dr. Richard Marsh for making the 9-ethylguanine structure available to us before publication and Dr. Leigh Clark for helpful discussions.

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(8) E. J. Rosa, Ph.D. Thesis, University of Washington, 1964.

(9) E. J. Rosa and W. T. Simpson, "Physical Processes in Radiation Biology," Academic Press, New York, N. Y., 1964, pp 43–49.

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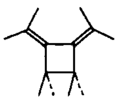
The Structures of Two Head-to-Head Allene Dimers

Sir:

The mechanism of allene dimerization has been studied for many years,[1] but stereochemical and spectroscopic techniques have not conclusively established the structures of the products. We have determined the structures of two model dimers by single-crystal X-ray diffraction. As far as we know, this is the first structural study of compounds containing the 1,2-dimethylenecyclobutane group (formed by head-to-head dimerization), shown below.



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(1) See T. L. Jacobs, J. R. McLenon, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.*, **91**, 6038 (1969), and references cited therein.

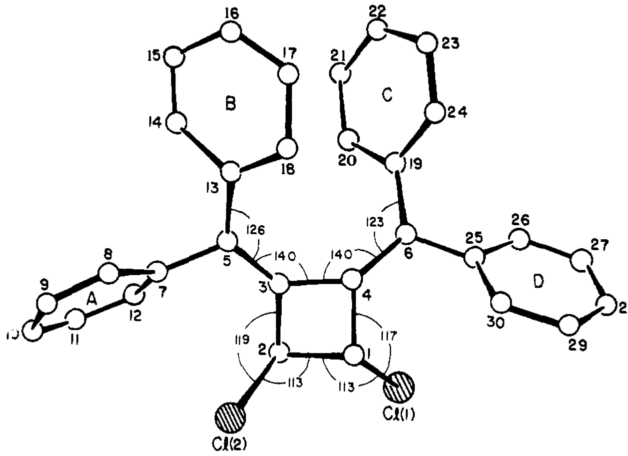

Figure 1. Projection of dimer I of 1,1-diphenyl-3-chloroallene upon the plane of atoms C(1), C(4), and C(3). The C–C and C–Cl bond lengths (ångströms, esd ±0.01) involving the dimethylenecyclobutane group are: Cl(1)–C(1), 1.79; Cl(2)–C(2), 1.80; C(1)–C(2), 1.55; C(2)–C(3), 1.54; C(3)–C(4), 1.48; C(1)–C(4), 1.52; C(4)–C(6), 1.35; C(3)–C(5), 1.34. Several important angles (degrees) are shown in the figure.

The structure of the major product I of the dimerization of 1,1-diphenyl-3-chloroallene is shown in Figure 1. Two major products are formed in the dimerization of 1-mesityl-3-chloroallene; the symmetrical isomer II was chosen for study and is shown in Figure 2.

The chlorine atoms in dimer I are trans, as suggested by a recent study of its ozonolysis products,[2] rather than cis as previously proposed.[3] In dimer II the chlorine atoms are also trans, and both mesityl groups are directed inward, confirming earlier assignments based on nmr chemical shifts.[4]

trans-1,2-Dichloro-3,4-bis(benzhydrylidene)cyclobutane (I) forms multifaceted deep yellow crystals in the space group $P\bar{1}$, a = 9.836 (14), b = 11.439 (7), c = 12.073 (8) Å, α = 105.43 (6), β = 112.95 (6), and γ = 92.17 (7)°.[5] There are two molecules in the unit cell. The R index is 0.074 for 2819 nonzero reflections collected with monochromatized Mo Kα radiation.

Neither the cyclobutane ring nor the butadiene portion of the molecule is planar. Each cyclobutyl carbon atom deviates from the best plane of the ring by 0.11 Å, while the four carbon atoms of the butadiene system are 0.04–0.09 Å away from its best plane.

Steric interactions of the inner phenyl groups are reflected in the angles about C(3), C(4), C(5), and C(6), and in the large twist angle about the central bond of the butadienyl group; the torsion angle C(6)–C(4)–C(3)–C(5) is 33°. Rings B and C are twisted to angles of 43 and 31° with the least-squares planes of the groups C(13)–C(7)–C(5)–C(3) and C(19)–C(25)–C(6)–C(4), respectively, and make an angle of 27° with each other. However, there is very little twist about the (formally) double bonds; the torsion angles are C(13)–C(5)–C(3)–C(4), 3°, and C(19)–C(6)–C(4)–C(3), −5°.

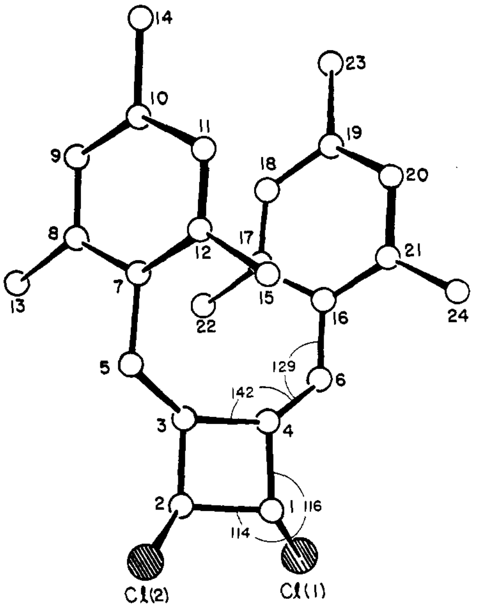

Figure 2. View of the dimer II of 1-mesityl-3-chloroallene along the c axis. The atoms C(1), C(4), C(6), C(16), etc., are related to C(2), C(3), C(5), C(7), etc., respectively, by the crystallographic twofold symmetry axis; thus the asymmetric unit consists of one-half molecule. The C–C and C–Cl bond lengths (ångströms, esd ±0.01) involving the dimethylenecyclobutane group are: Cl(1)–C(1), 1.80; C(1)–C(2), 1.54; C(1)–C(4), 1.53; C(3)–C(4), 1.47; C(3)–C(5), 1.36. Several important angles (degrees) are shown in the figure.

The angles about C(2) and C(1) probably demonstrate the interaction of the chlorine atoms with the outer phenyl rings. Rings A and D make angles of −54 and 48° with the least-squares planes C(13)–C(7)–C(5)–C(3) and C(19)–C(25)–C(6)–C(4) referred to above. The Cl(1)–C(1)–C(2)–Cl(2) torsion angle is 105°.

If a bond dipole moment of 1.90 D is chosen for the C–Cl dipoles[6] the contribution of the chlorines to the dipole moment of I would be 2.14 D. This is close to the value of 2.16 D reported recently by Dehmlow[2] for I. For a model of I having a planar four-membered ring and Cl–C–C angle of 113° Dehmlow calculated a contribution of 1.44 D for trans chlorines. He measured a dipole moment of 0.72 D for 1,2-bis(benzhydrylidene)cyclobutane, the parent hydrocarbon of I, and this value added to 1.44 gave him 2.16 D as the calculated dipole moment of I. One would not expect the contribution of the rest of the structure in I to the dipole moment to be the same as the dipole moment of the hydrocarbon, especially since rings A and D are so far from coplanar with the 1,3-butadiene system as a result of interference with the chlorines. It is curious that 2.86 D, the sum of 2.14 D contribution of the chlorines and 0.72 D for the hydrocarbon, is close to 2.81 D, the earlier value measured for the dipole moment of I.[3]

Pale yellow crystals of the dimer II of 1-mesityl-3-chloroallene belong to the monoclinic system. The cell parameters are a = 15.966 (1), b = 14.875 (1), c = 9.304 (1) Å, β = 109.833 (9)°. The space group is $C2/c$ with two molecules per unit cell; thus the asymmetric unit contains only one-half molecule. The R index is presently 0.090 for 1173 nonzero reflections collected with Cu Kα radiation.

The structures of dimers I and II are quite similar; all bond lengths (see legends, Figures 1 and 2) in the dimethylenecyclobutane portion of II are within two

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[2] E. V. Dehmlow, *Tetrahedron Lett.*, 4283 (1969).

[3] P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 2707 (1963).

[4] O. J. Muscio, Jr., and T. L. Jacobs, *Tetrahedron Lett.*, 2867 (1969).

[5] Esd's, in parentheses, are right adjusted to the least significant digit of the preceding number.

[6] J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955.

standard deviations of those in I. However, the removal of the outer phenyl rings and the substitution of bulkier mesityl groups for phenyl groups in the inner positions upon going from I to II result in two large differences in twist angles. The torsion angle about the central bond in the butadiene portion [C(5)–C(3)–C(4)–C(6)] is much smaller in II (18°) than in I (33°) while the best plane of the mesityl ring makes an angle of 54° with the C(7)–C(5)–C(3) plane compared to 43 and 31° in I. There are also slight differences in bond angles at carbon atoms C(4), C(5), and C(1) consistent with the different substituents in I and II.

The determination of the structures of I and II establishes these compounds as models whose spectra and dipole moments may assist in the assignment of structures to other allene dimers. The isomer of II obtained from it by iodine-catalyzed rearrangement must also have trans chlorines (the mesityl groups are outward rather than inward), and the other 1,2-dichloro-3,4-bis(2,4,6-trimethylbenzylidene)cyclobutane, which has one mesityl inward and one outward, probably has trans chlorines as well on the basis of the nmr signals of the ring protons.[4]

The principal dimer of 1-chloro-3-methyl-1,2-butadiene was originally assigned a structure with trans chlorines on the basis of ozonization to yield *dl*-2,3-dichlorosuccinic acid. However, a preliminary report by Bertrand and coworkers[7] suggested that some of the meso acid might also be formed. The dipole moment observed for this dimer, 2.63 D, was in poor accord with the values calculated for the structure with trans (1.44 D) or cis chlorines (3.50 D). If the ring structure of this dimer resembles that of I with an expected contribution of 2.14 D for the C–Cl bonds, the observed value and the value for the trans structure are in much better agreement. The definitive paper from Bertrand's group has now appeared[8] and there is agreement that ozonization of this dimer yields only *dl*-2,3-dichlorosuccinic acid and none of the meso isomer. The trans structure thus appears to be established.

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[8] R. Maurin, G. Leandri, and M. Bertrand, *Bull. Soc. Chim. Fr.*, 530 (1971).

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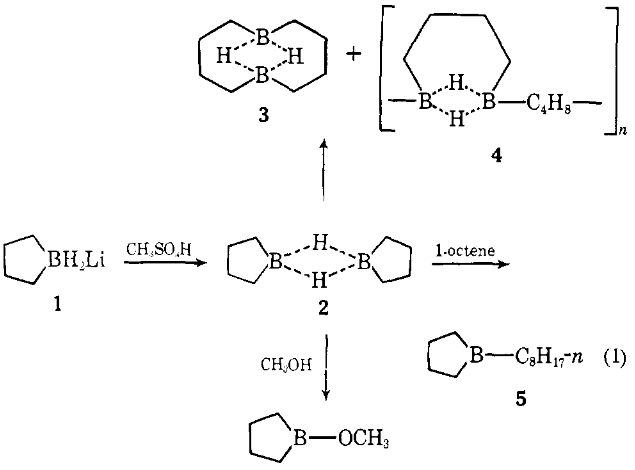
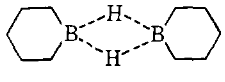
Bisborolane. A Highly Elusive Bisboracyclane

Sir:

The reaction of lithium tetramethyleneborohydride (**1**) with methanesulfonic acid produces the hitherto elusive bisborolane (**2**) as a fugitive species. In the absence of trapping reagents, the intermediate is rapidly transformed into 1,6-diboracyclodecane (**3**) and a polymer (**4**). However, addition of 1-octene or methanol immediately following the generation produces *B*-(*n*-octyl)borolane (**5**) or *B*-methoxyborolane (**6**), respectively. Thus, the results of these reactions (eq 1) provide the first unambiguous demonstration of the independent existence of bisborolane (**2**).



Bisborinane (**7**) is a thermally stable bisboracyclane.[1] However, the five-membered analog, bisborolane (**2**), has been highly elusive. Thus, the hydroboration of



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1,3-butadiene does not yield **2** as a final product.[2] Instead, the product is a polymer largely represented by **4**, which undergoes methanolysis rapidly and yet hydroborates olefins only sluggishly at room temperature.[2a] On heating, **4** is converted to an unusually stable tetraalkyldiborane, **3**, which reacts neither with olefins nor with methanol at detectable rates at 25°.[2b]

Earlier, Köster[3] assigned the bisborolane structure **2** to the product obtained in the reduction of *B*-chloroborolane with lithium aluminum hydride. However, the properties reported for the product are identical with those of the highly stable species obtained in the hydroboration of 1,3-butadiene,[4] recently shown to have the structure **3**.[2b,5] Therefore, the reduction product isolated must also be **3**. The first indication that bisborolane (**2**) must be an active hydride species capable of reacting readily with olefins was realized in the reduction of *B*-methoxyborolane (**6**) with lithium aluminum hydride in the presence of olefins.[6] In this reaction, the olefins underwent rapid hydroboration to form the corresponding *B*-alkylborolanes in high yields. These results strongly support the formation of **2** as an intermediate capable of rapid hydroboration of olefins. However, the synthesis of free bisborolane as a distinct species with independent existence has not yet been demonstrated.

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[2] (a) H. C. Brown, E. Negishi, and P. L. Burke, *J. Amer. Chem. Soc.*, **93**, 3400 (1971); (b) E. Breuer and H. C. Brown, *ibid.*, **91**, 4164 (1969).

[3] R. Köster and G. Benedikt, *Angew. Chem.*, **75**, 346 (1963).

[4] (a) R. Köster, *ibid.*, **72**, 626 (1960); (b) R. Köster, *Advan. Organometal. Chem.*, **2**, 257 (1964).

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[6] H. C. Brown, E. Negishi, and S. K. Gupta, *ibid.*, **92**, 2460, 6648 (1970).