tendency for these moieties to occupy nonadjacent positions in carborane polyhedra. Similar arguments have been proposed or considered for the C,C'-dimethyl derivative of $C_2B_6H_8$[2b] and $B_8H_8^{2-}$,[4] both of which have unexpectedly simple ^{11}B nmr spectra.

Compound I is thermally stable to at least 250° and is apparently unreactive with air. However, its conversion to 2,4-$C_2B_5H_7$ [dicarba-*closo*-heptaborane(7)] is strongly favored thermodynamically, as shown in two experiments. In the electron-impact mass spectrometer, I is converted to $C_2B_5H_7$ and no evidence of the original three-carbon species is seen. Secondly, pyrolysis of I at 400° generates $C_2B_5H_7$ in virtually 100% yield.[8] Presumably, the driving force in these processes arises from the considerable thermal stability of the $C_2B_5H_7$ polyhedron, although the presumed presence of an unshared electron pair on $C_3B_5H_7$ is also likely to be a factor contributing to increased reactivity of the molecule.

The synthesis of I from silylcarboranes is difficult to rationalize at this point, although unexpected findings of this kind are not particularly unusual in gas-phase borane reactions. An earlier result which may be related to the present work is the formation of small closo carboranes from dimethylsilane and pentaborane-(9).[9] Such reactions could involve methyne (CH) insertion into the borane cage, but more exotic mechanisms, such as the formation and subsequent disproportionation of unstable closo silacarborane intermediates, are also conceivable. Further studies of the $C_3B_5H_7$ system are in progress and will be reported at a later date.

Acknowledgments. We thank Mr. Richard Torian and Dr. Roger Upham for assistance in obtaining chemical ionization mass spectra. This work was supported by the Office of Naval Research.

(8) The fate of the ejected carbon atom has not yet been established, partly owing to the small scale of the pyrolysis experiments. However, no volatile products other than 2,4-$C_2B_5H_7$ have been detected by glpc analysis.
(9) W. A. Ledoux and R. N. Grimes, *J. Organometal. Chem.*, **28**, 37 (1971).
(10) On sabbatical leave from Lake Forest College, Lake Forest, Ill., 1970-1971.

Martin L. Thompson,[10] Russell N. Grimes*
*Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901*

Polarization of Electronic Transitions in 9-Ethylguanine

Sir:

Knowledge of the electric dipole transition moments of the DNA bases is of interest because they enter, as matrix elements, into theoretical treatments of optical properties and energy transfer in DNA. The transition moment directions for bands between 270 and 230 nm for all the principally occurring DNA and RNA bases have been experimentally assigned except for guanine.[1]

In this communication we wish to report the results of polarized specular reflectance measurements of single crystals of 9-ethylguanine which, in conjunction with

(1) For references, see T. O. Lewis and W. A. Eaton, *J. Amer. Chem. Soc.*, **93**, 2054 (1971).
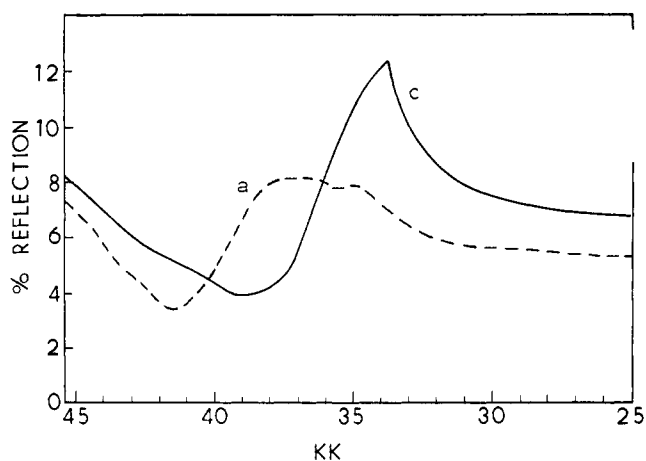

Figure 1. Polarized specular reflectance for the *ac* face of a single crystal of 9-ethylguanine: (———) light polarized along the *c* axis (optic axis), (- - -) light polarized perpendicular to the optic axis.

the recently solved crystal structure,[2] yield information concerning the absolute directions of the transition moments for the first two strong transitions of the guanine chromophore. These two bands have maxima at *ca.* 270 nm (ϵ_{max} ~9000) and 253 (~13,000)[3] and will hereafter be referred to as I and II, respectively.

The crystals of 9-ethylguanine were obtained by slow evaporation of methanol solution at 20°. Experimental details regarding measurement of the reflection spectra are as described previously.[4]

The essential details of the crystal structure are as follows.[2] The crystal system is tetragonal with space group $P_{4_12_12}$. Thus all information regarding electric dipole transition moments is obtainable from measurements on a single face parallel to the *c* axis. It turns out that there are only four electromagnetically distinct molecules per unit cell when viewing the *ac* face. Two of these may be considered as having their planes parallel to *ac* and the other two as having their planes parallel to *bc*. (Actually, all the molecules have their planes tipped 5° away from the *c* axis. Ignoring this does not significantly affect analysis of the data.) The arrangement of the molecules in the crystal is such that a vector drawn between atoms N_2 and C_8 (numbering as in Figure 2) is with in 2° of being perpendicular to the *c* axis (optic axis) for every molecule. It follows that the N_2-C_8 vector is parallel to *a* for half the molecules and parallel to *b* for the other half. It also follows that the in-plane vector perpendicular to N_2-C_8 is within 2° of being parallel to *c* for every molecule.

Turning now to Figure 1, we see the specular reflectance taken on the *ac* face. When the light is polarized along the *c* axis, there is only one "anomaly" in the reflection curve. It is centered at 36 kK (278 nm) and therefore is caused by transition I. Evidently, the transition moment of II is nearly perpendicular to *c* for every molecule and thus lies close to the N_2-C_8 direction.

When the light is polarized along the *a* axis, one indeed sees II manifested strongly by an anomaly centered at 39.5 kK (253 nm). That II does not appear as

(2) R. Destro and R. E. Marsh, manuscript in preparation.
(3) (a) P. R. Callis, E. J. Rosa, and W. T. Simpson, *J. Amer. Chem. Soc.*, **86**, 2292 (1964); (b) L. B. Clark and I. Tinoco, Jr., *ibid.*, **87**, 11 (1965).
(4) P. R. Callis and W. T. Simpson, *ibid.*, **92**, 3593 (1970).
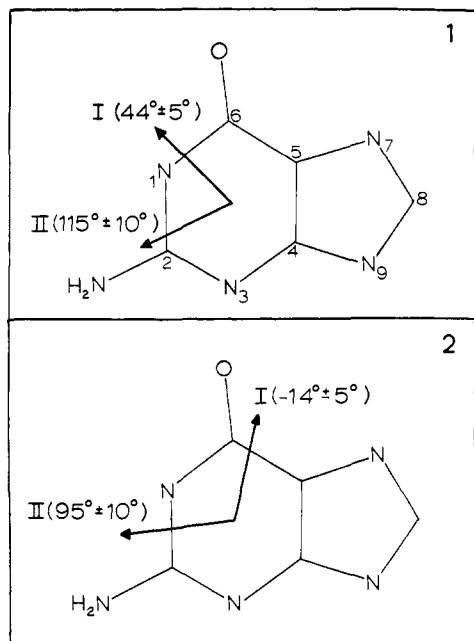
Figure 2. The two possible assignments of transition moment directions in 9-ethylguanine as deduced from combined information from polarized specular reflectance measurements on single crystals and from fluorescence polarization. I denotes the 270-nm band and II the 253-nm band. The ambiguity may be 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_8 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

(5) H. Devoe and I. Tinoco, *J. Mol. Biol.*, **4**, 518 (1962).
(6) A. H. Kalantar and A. C. Albrecht, *Ber. Bunsenges. Phys. Chem.*, **68**, 361 (1964).

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.

(7) L. Clark, private communication.
(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.

Patrik R. Callis*

Department of Chemistry, Montana State University
*Bozeman, Montana 59715*

Bruno Fanconi, William T. Simpson

Department of Chemistry and Institute of Molecular Biology
University of Oregon, Eugene, Oregon 97403

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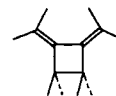
(1) See T. L. Jacobs, J. R. McLenon, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.*, **91**, 6038 (1969), and references cited therein.