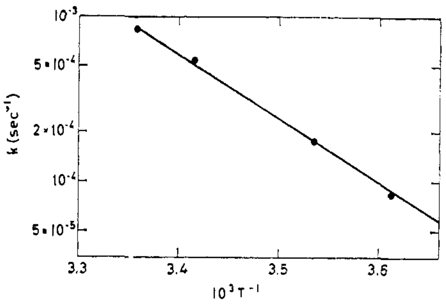

Figure 4. Semilogarithmic plot of the exchange rate constant of poly(N-vinylacetamide) at pD 4.1 as a function of reciprocal temperature.

rates could, however, be explained by assuming that the local concentration of water (and therefore of D_3O^+ and OD^-) in the environment of the amide group is lower, on the average, in solutions of macromolecules than in solutions of low molecular weight compounds. We tentatively suggest that the exchange rates be explained in terms of the reaction mechanism originally suggested for the exchange of hydrogen atoms in protein molecules.[2a,20] This mechanism assumes that a macromolecule in solution undergoes statistical fluctuations, changing with time the relative positions of its constituent groups, *i.e.*, changing conformation. In some conformations a given amide group is freely exposed to the solvent, and the rate constant of exchange of its hydrogen atom is similar to that of an amide group in a corresponding low molecular weight compound. In other conformations the group considered is protected by other parts of the macromolecule from exposure to the solvent, and, therefore, prevented from exchanging its hydrogen atom. According to this mechanism the ratio $k_{\text{polymer}}/k_{\text{monomer}}$ is a measure of the fraction of time spent, on the average, by the amide groups of the polymer in free contact with the solvent. It is a consequence of this mechanism that the activation energy of the exchange reaction is similar for a polymer and for the corresponding monomer. Figure 4 shows an Arrhenius plot of the rate constants measured for poly(N-vinylacetamide) at pD 4.1. The straight line drawn corresponds to an activation energy for the acid-catalyzed reaction of 18 kcal/mol, in satisfactory agreement with the value of 17 kcal/mol reported by Klotz and Frank[18] for the corresponding reaction of N-methylacetamide.

We take this study of the H–D exchange in solutions of poly(N-vinylacetamide) as supporting the idea that kinetic investigations of the hydrogen exchange in macromolecular solutions may offer information about the accessibility of the amide groups of the macromolecules to the solvent, or about the extent to which the macromolecules are "freely drained." The data presented in Table I suggest that the amide groups of poly(N-vinylacetamide) spend about 5% of the time exposed to the solvent. The inaccessibility of the amide groups to the solvent need not result from the overall conformation of the macromolecule, but may be an effect of interactions among neighboring groups.

Acknowledgments. One of the authors (Aa. H.) wishes to thank the Carlsberg Foundation for grants for experimental equipment used in this investigation. The skilled technical assistance of Mrs. Gerda Christensen is gratefully acknowledged.

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(20) Aa. Hvidt, *C. R. Trav. Lab. Carlsberg*, 34, 299 (1964).

Nonplanarity in Hexafluorobutadiene as Revealed by Photoelectron and Optical Spectroscopy

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Contribution from the Bell Telephone Laboratories, Murray Hill, New Jersey 07974.
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Abstract: Comparison of the photoelectron spectra of the perfluorinated diene $F_2C{=}CF{-}CF{=}CF_2$ and its hydrogen analog, butadiene, demonstrates that the interaction between the two ethylenic groups in the former is only one-third that in the latter, whereas in $F_2C{=}CH{-}CH{=}CF_2$, the full interaction is observed. On this basis it is suggested that the carbon skeleton of hexafluorobutadiene is nonplanar. In support of this, the optical spectra of butadiene and 1,1,4,4-tetrafluorobutadiene are of the usual sort, each with a very strong $N \rightarrow V_1$, but very weak $N \rightarrow V_2$ transition. The $N \rightarrow V_2$ transition in hexafluorobutadiene, however, is the stronger of the two, and it is concluded on the basis of a simple intramolecular exciton calculation that the observed $(N \rightarrow V_1)/(N \rightarrow V_2)$ intensity ratio is consistent with a cisoid molecular structure, the dihedral angle being 42 ± 15°, in agreement with a subsequent electron diffraction value of 47.60 ± 0.58°.

Questions regarding the conformations about the single and double bonds of substituted 1,3 dienes are of increasing interest, as modern experimental methods put the answers more and more within reach. In this paper, we report the results of an investigation of the optical and photoelectron spectra of hexafluorobutadiene, directed toward determining its conformation in the gas phase. For comparison, the molecules butadiene and 1,1,4,4-tetrafluorobutadiene, both of known conformation, were also investigated.

Butadiene itself exists in the *trans*-planar configuration in the gas phase, possibly in equilibrium with a few per cent of the *cis* (planar?) isomer,[1] though there is no direct spectroscopic proof of this.[2] The evidence for the structure of 1,1,4,4-tetrafluorobutadiene is no less compelling than that for *trans*-butadiene itself,[3] for the Raman, infrared,[4] and microwave[5] spectra lead one quite naturally to a *trans*-planar structure. The predominant conformation in hexafluorobutadiene is not as readily deduced, for Albright and Nielsen[6] found numerous coincidences of Raman and infrared lines, indicative of a noncentrosymmetric structure, and from this proposed a *cis*-planar conformation, whereas Conrad and Dows[4] comment on the disadvantageous overlap of fluorine atoms in the *cis*-planar form. Recent nmr experiments on this molecule also have been interpreted as indicating a nonplanar structure.[7]

The four π electrons of a 1,3-diene system occupy the two lowest π MO's in the ground state. Inasmuch as *cis*- and *trans*-planar dienes differ only in the π-electron interactions between the AO's on carbon atoms C_1 and C_4, one expects very little difference in the energetics of the π electrons in these two conformations. Indeed, extensive calculations have shown that the lowest energy π-electron excitations in *cis*- and *trans*-butadiene differ by only 0.5 eV at most,[8–10] and that their first ionization potentials differ by only 0.1 eV.[10,11] At the most naive level, this is a consequence of the fact that the overlap of the two ethylenic double bonds, and the consequent π_1–π_2 splitting, are virtually identical in the *cis*- and *trans*-planar conformations.

However, when the two ethylenic groups of butadiene are nonplanar, then the π-electron energies will be very different from those of the two planar conformers. In particular, as the molecule is twisted about the central bond, the two occupied π MO's, π_1 and π_2, collapse toward one another, as they both converge upon the π-orbital energy of the isolated component monoolefin. Such orbital energies are readily obtained from the photoelectron spectrum of the molecule in question. As the splitting between the occupied π levels decreases on twisting, the energy of the lowest $\pi \rightarrow \pi^*$ ($\pi_2 \rightarrow \pi_3$, $N \rightarrow V_1$) optical excitation increases as it moves toward that of the corresponding olefin. Furthermore, the first band in the optical spectrum of *trans*-planar dienes ($N \rightarrow V_1$) is strongly allowed and the second ($N \rightarrow V_2$) is LaPorte forbidden, whereas in nonplanar olefins, both bands are allowed, with the second actually stronger than the first in a particular range of twist angle. It is apparent from this that the π_1–π_2 splitting in the photoelectron spectrum and the $N \rightarrow V_1$ and $N \rightarrow V_2$ energies and especially intensities in the optical spectrum of hexafluorobutadiene are intimately related to the conformation about its central C–C bond in the ground state.

Experimental Section

The hexafluorobutadiene used here was a commercial material having an infrared spectrum identical with that reported in the literature.[6] The butadiene was research grade, with stated purity of 99.89%, and the 1,1,4,4-tetrafluorobutadiene was a gift from Dr. S. L. Manatt, Jet Propulsion Laboratory, Pasadena, Calif. Photoelectron spectra were recorded using a high-resolution, 127° electrostatic analyzer with both He I (21.22 eV) and He II (40.82 eV) excitation. Construction of an instrument of this type is described in ref 12. Optical spectra were recorded using a 1-m normal incidence spectrometer, rare gas continuum lamps, LiF-windowed cells, and photoelectric recording.

Photoelectron Spectra

Before discussing the photoelectron spectra, it will be useful to describe the effect of substituting fluorine for hydrogen on the molecular orbital energies. We have found in a large number of unsaturated systems containing a relatively large number of fluorine or hydrogen atoms, that the inductive effect of fluorine acts specifically on the σ molecular orbitals, while leaving the π orbitals almost untouched.[13] Specifically, in the pairs of C_xH_y–C_xF_y molecules having $y > x$ which we have studied, the π-electron IP's are virtually identical in the two molecules, whereas the corresponding σ IP's are uniformly higher by approximately 3 eV. This is the so-called "perfluoro effect" in photoelectron spectroscopy, and will be of value here in interpreting the diene spectra.

The He I photoelectron spectrum of butadiene is shown in Figure 1. It is in agreement with that already published by Eland.[14] At present, our interest extends only to the first few ionization potentials, the first of which, at 9.06 eV, is undoubtedly due to removal of an electron from the $1b_g(\pi_2)$ orbital. The assignment of the second band at 11.55 eV (vertical) is less certain, for semiempirical calculations[15] place the highest σ level, $7a_g$, somewhat above the second

Table I. Comparison of the Observed and Calculated IP's of *trans*-Butadiene

Orbital	0.92KT[a]	Vertical IP	Adiabatic IP
$1b_g$ (π)	8.96	9.06 (7)	9.06 (7)
$1a_u$ (π)	11.94	11.47, 12.23	11.22
$7a_g$ (σ)	12.87		
$6b_u$ (σ)	14.24	13.5	12.99
$6a_g$ (σ)	14.37	13.9	
$5b_u$ (σ)	16.52	15.28	≃15.0
$5a_g$ (σ)	16.62	16.1 (?)	
$4b_u$ (σ)	19.40	18.0	17.5
$4a_g$ (σ)	20.98	19.1	
$3b_u$ (σ)	25.56	22.4[b]	21.2[b]
$3a_g$ (σ)	27.76		

[a] Ionization potentials (eV) computed using the Koopmans' theorem (KT) results of ref 10, multiplied by the empirical factor 0.92, as recommended in ref 16 for this type of calculation. [b] Values taken from the He II spectrum.

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(1) J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946).

(2) See, for example, D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*, **17**, 163 (1962).

(3) A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958).

(4) R. M. Conrad and D. A. Dows, *Spectrochim. Acta*, **21**, 1039 (1965).

(5) R. A. Beaudet, *J. Amer. Chem. Soc.*, 87, 1390 (1965).

(6) J. C. Albright and J. R. Nielsen, *J. Chem. Phys.*, **26**, 370 (1957).

(7) S. L. Manatt and M. T. Bowers, *J. Amer. Chem. Soc.*, **91**, 4381 (1969).

(8) R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, 18, 1338 (1950).

(9) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc. London, Sect. A*, 68, 601 (1955).

(10) R. J. Buenker and J. L. Whitten, *J. Chem. Phys.*, **49**, 5381 (1968).

(11) M. J. S. Dewar and S. D. Worley, *ibid.*, **49**, 2454 (1968).

(12) D. W. Turner, *Proc. Roy. Soc., Ser. A*, **307**, 15 (1968).

(13) C. R. Brundle, M. B. Robin, D. B. Neumann, and H. Basch, manuscript in preparation.

(14) J. H. D. Eland, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 471 (1969).

(15) See, for example, M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw Hill, New York, N. Y., 1969, p 464.

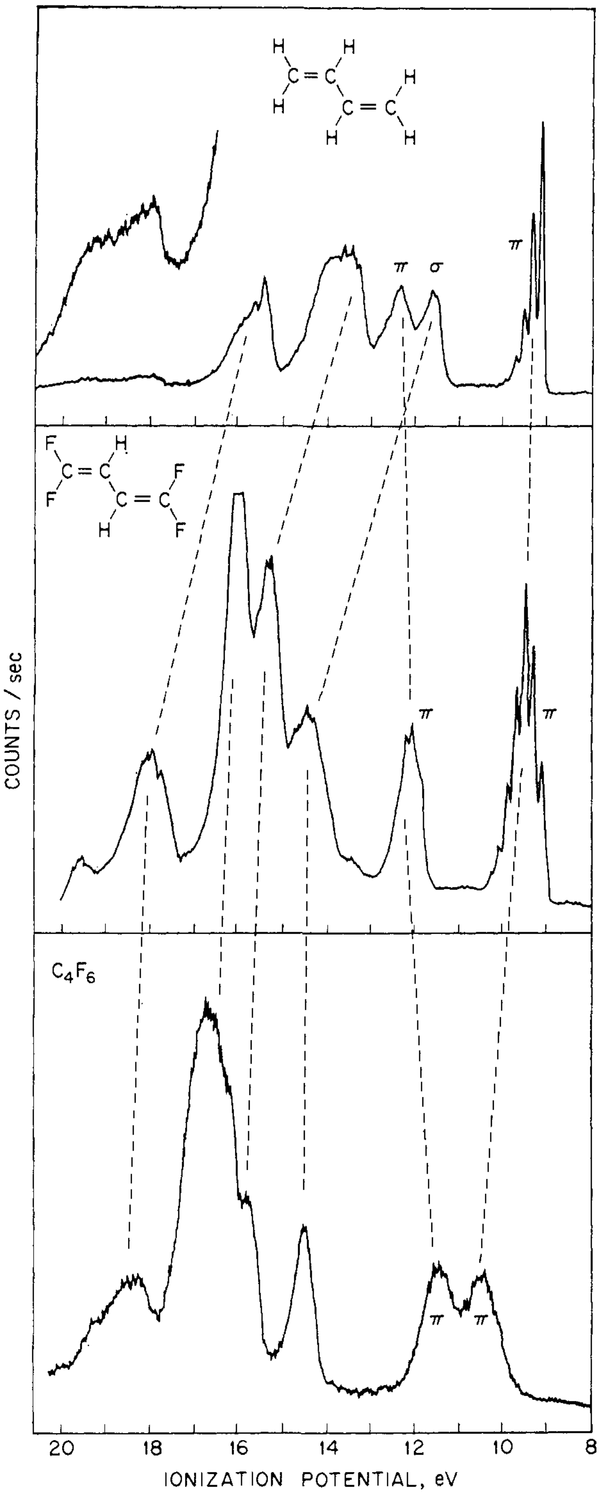

Figure 1. Comparison and correlation of the He I photoelectron spectra of butadiene, 1,1,4,4-tetrafluorobutadiene, and hexafluorobutadiene.

π level, $1a_u(\pi_1)$, whereas the more rigorous *ab initio* calculation of the butadiene orbital structure[10] reverses this order. It is in situations such as this that the perfluoro effect can sometimes be used to good advantage.

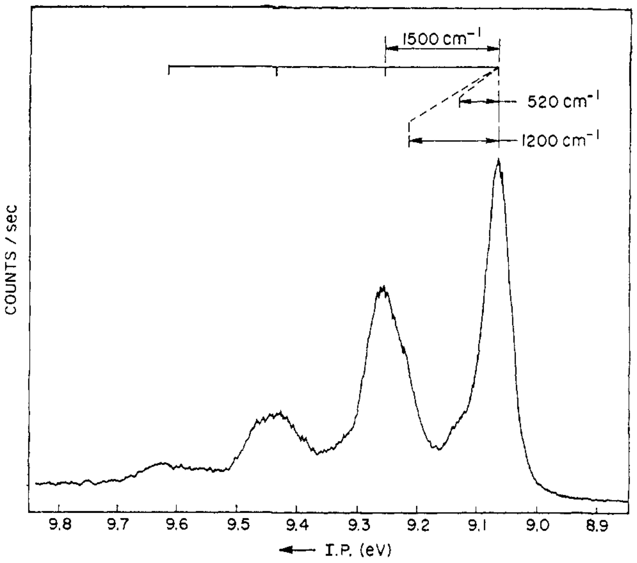

Figure 2. Details of the first band of the He I photoelectron spectrum of butadiene.

In Table I, a compilation of the bands found in the photoelectron spectrum of butadiene is presented, along with the Koopmans' theorem approximation to these values calculated by Buenker and Whitten[10] and modified empirically by multiplication by 0.92.[16] One sees in these a rather good agreement with experiment for the lower bands, with successively poorer agreement as one goes deeper into the molecule. If the Buenker and Whitten wave function is near Hartree–Fock, then the hoped-for cancellation of correlation energy and reorganization energy errors[16] implicit in Koopmans' theorem is less fulfilled for the deeper levels, with the reorganization energy error becoming progressively dominant. If, however, there is only one ionic state in the 15–16.5-eV region, so that the $5a_g$ ionization potential is at 18.0 eV, rather than at 16.1 eV, then the regularity of the computed discrepancy will be disturbed at this point. In either event, the calculation outwardly seems to be adequate for the lower excitations, and there is nothing to suggest that the ordering of the first four or five bands is not as predicted by Buenker and Whitten's orbital energies. However, in our final interpretation of the photoelectron spectra, we will conclude that the correct ordering of the first three ionized states of butadiene is instead Π,Σ,Π, as given by the semiempirical calculation and Koopmans' theorem.

The most prominent aspect of the first photoelectron band of butadiene is the short progression with spacing 1500 cm^{-1}, Figure 2. A natural candidate for this mode would be ν_4', the totally symmetric double bond stretching vibration, reduced from 1643 cm^{-1} in the neutral molecule ground state.[17] Intervals of 520 and 1200 cm^{-1} are also evident which were not reported by Eland.[14] If the molecule–ion is planar and centrosymmetric, then only a_g vibrational levels will appear in the vibronic envelope. In that case, the 520-cm^{-1} interval is most likely the in-plane C=C—C angle bending mode (513 cm^{-1} in the ground state), while the 1200-cm^{-1} vibration would appear to be the central bond C—C stretch (1205 cm^{-1} in the ground state). That C=C stretching should be excited strongly and C—C stretching weakly is reasonable, since the transi-

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[16] H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, 51, 52 (1969).

[17] L. M. Sverdlov and N. V. Tarasova, *Opt. Spectrosk.*, 9, 159 (1960); R. K. Harris, *Spectrochim. Acta*, 20, 1129 (1964).

tion involves removal of an electron from an orbital which is strongly C═C bonding and weakly C—C antibonding.

If the perfluoro effect works as expected for 1,1,4,4-tetrafluorobutadiene, then the two C═C π-electron ionizations in the tetrafluoro compound will appear at almost exactly the same energies as observed in butadiene, whereas the σ excitations will have moved 2–3 eV to higher energies and a strong, unresolved feature will appear at about 17 eV, due to the fluorine lone-pair IP's. Comparison of the spectra of Figure 1 (and Tables I and II) shows that such a simple pattern is readily uncovered. The first π level stays at exactly the same energy though its band shape changes somewhat. If the second IP of butadiene is taken to be the second π level, an increase in IP of 0.5 eV (vertical) occurs on going to the tetrafluoro compound. In our experience this is almost too large a shift for a "perfluoro" π shift. If instead the third IP is taken as the second π level, a small decrease of 0.2 eV occurs on fluorination. Also with this assignment for butadiene, π,σ,π, the two π levels are almost symmetrically split about the center of gravity of the ethylene π level at 10.7 eV.[14]

Table II. Observed IP's of the Fluorinated Butadienes

Tetrafluorobutadiene Vertical IP	Tetrafluorobutadiene Adiabatic IP	Hexafluorobutadiene Vertical IP	Hexafluorobutadiene Adiabatic IP
9.38	8.98	10.4	≃9.5
12.04	11.55	11.4	
14.5	≃13.5	14.45	14.0
15.3		15.75	15.3
16.0		16.3	
		16.6	
18.0	17.4	18.8	≃18.0
19.6[a]	19.2[a]	19.4[a]	
21.0[a]	20.7[a]	20.7[a]	
21.9[a]		21.9[a]	21.5[a]
		22.8[a]	

[a] Values taken from the He II spectrum.

The vibrational structure evident on both π bands in the 1,1,4,4-tetrafluorobutadiene is the ν_4 C═C stretching mode (which might be expected for the removal of a π electron). It has a frequency of 1600 cm^{-1} in the first band and 1450 cm^{-1} in the second. The correlation lines drawn in on Figure 1 illustrate how the IP's of the σ levels have increased uniformly by 2.5–3 V on fluorination. The intense band at about 16 eV is attributed to the fluorine lone-pair ionizations.

Returning now to the photoelectron spectrum of hexafluorobutadiene, Figure 1 and Table II, we immediately recognize the two transitions at 10.40 and 11.42 eV (vertical) as coming from the two occupied π orbitals, but with an energy separation only one-third that of the corresponding orbitals in butadiene and 1,1,4,4-tetrafluorobutadiene. This is a clear signal that the two halves of the molecule have been significantly decoupled presumably by twisting about the central C–C bond. An estimate of the dihedral angle could conceivably be made utilizing the observed π_1–π_2 split and a molecular orbital theory which includes π and σ orbitals explicitly. However, even if we were to do this, the result would be ambiguous, for the π-orbital splittings are very nearly identical for *cis* and *trans* dienes twisted by the same angle from their respective planar conformations. Fortunately, the electronic spectrum contains the additional information required to settle the question of conformation and dihedral angle. Note also that even if the orbital ordering in butadiene really is π,π,σ, the qualitative conclusion as regards the weaker π-electron interaction in hexafluorobutadiene is still valid. The fact that both the π levels of hexafluorobutadiene and 1,1,4,4-tetrafluorobutadiene are approximately symmetrically split about the C_2F_4 value (also at 10.7 eV,[13] as in ethylene), and that the π levels of hexafluorobutadiene are collapsing toward this value (actually 10.9 eV is the mean value of the two π bands), seems to indicate that the π levels of butadiene would be expected to be symmetrical about 10.7 eV, as is the case for the π,σ,π assignment.

Unlike butadiene and 1,1,4,4-tetrafluorobutadiene, the photoelectron bands of hexafluorobutadiene show no signs of any vibrational structure. About all one can say here is that, since the lowest state of the ion cannot be broadened by rapid relaxation to lower states, and since the parent ion $C_4F_6^+$ is found mass spectrometrically,[18] thereby ruling out broadening due to dissociation, the lack of resolvable features in at least the first band is possibly due to the excitation of numerous low-frequency motions. A similar comment applies to the lack of vibrational structure in the optical spectrum of this diene.

The σ-level bands undergo relatively little change on replacing the final two hydrogens by fluorine, as can be seen in Figure 1 and Table II. The fluorine lone-pair region becomes broader, as might be expected for the addition of nonterminal fluorine atoms.

Optical Spectra

The spectra of the three dienes of interest are shown in Figure 3. The strong band in butadiene centered at 2100 Å is the N → V_1 transition and has an oscillator strength, f_1, of about 0.4. The companion N → V_2 band in butadiene is thought to lie near 1750 Å[19] and is symmetry forbidden. The sharp features in the 2000–1550-Å region are Rydberg excitations and do not concern us. As expected, the π-electron spectrum of 1,1,4,4-tetrafluorobutadiene is very much like that of butadiene itself, having an intense N → V_1 band at 2000 Å followed by sharp Rybderg bands and, supposedly, a weak N → V_2 absorption around 1650 Å. In sharp contrast to these, the hexafluorobutadiene spectrum shows two prominent N → V excitations, at 1970 and 1640 Å, with the second more intense than the first.

For our purposes, the optical spectra of the dienes can best be treated using the resonance force model of Simpson,[20] since this model expresses the $\pi \rightarrow \pi^*$ intensities in a simple geometrical manner. In particular, using a product-type wave function for the ground state, and the excitonic interaction between locally excited olefin groups in the upper states, one finds that the ratio of the oscillator strengths of the

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(18) F. N. Chelobov, S. S. Dubov, M. V. Tikhomirov, and M. I. Dobrovitskii, *Zh. Fiz. Khim.*, **40**, 1400 (1966).

(19) W. C. Price and A. D. Walsh, *Proc. Roy. Soc., Ser. A*, **174**, 220 (1940).

(20) W. T. Simpson, *J. Amer. Chem. Soc.*, **77**, 6164 (1955).

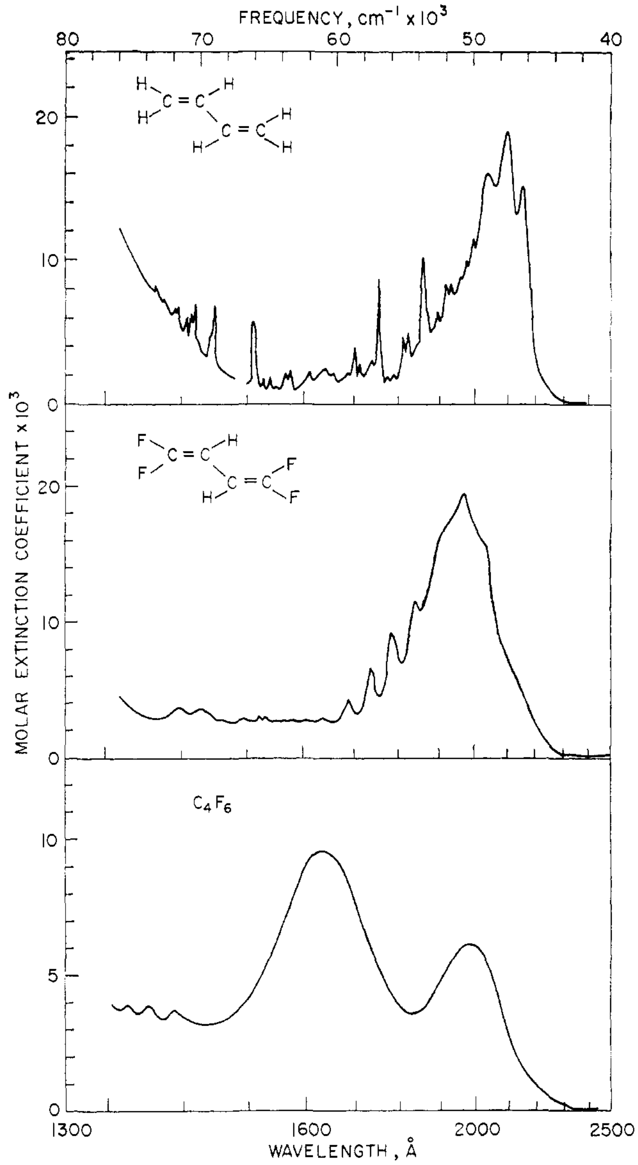

Figure 3. Optical spectra of gaseous butadiene, 1,1,4,4-tetrafluorobutadiene, and hexafluorobutadiene.

first two π-electron excitations in a twisted diene has the especially simple form

$$\frac{f_2}{f_1} = \frac{3 + 3 \cos \theta}{5 - 3 \cos \theta} \qquad (1)$$

where θ is the dihedral angle between the two olefinic groups, and equals zero for the *cis*-planar conformer. One sees from eq 1 that f_2 is zero for a *trans*-planar diene, and that all *trans* conformers and those *cis* conformers having θ greater than 70.5° will have an f_2/f_1 ratio smaller than 1.0. On the other hand, a rough estimation of f_2 and f_1 from the hexafluorobutadiene spectrum, Figure 3, leads to a ratio of 1.9, unambiguously showing the molecule to have a *cisoid* conformation. Less certain is the quantitative prediction of 42° for the dihedral angle. Allinger and Miller[21] have treated the problem of the $N \rightarrow V$ oscillator strengths in twisted butadiene using a π-electron MO theory, and report results resembling ours, in that they find that nonplanar-*cis* dienes do have $N \rightarrow V_2$ bands (in their notation, $N \rightarrow V_3$ bands) which are more intense than the lowest $N \rightarrow V_1$ band, whereas the reverse holds for the nonplanar-*trans* dienes.

As expected, the wavelength of the $N \rightarrow V_1$ band maximum in hexafluorobutadiene is somewhat shorter than that of planar *trans*-butadiene. However, this cannot be taken as strong support for our ideas, since the $\pi \rightarrow \pi^*$ spectra of planar fluorinated olefins[22] also show a strong blue shift as successive hydrogens are replaced by fluorine atoms. The blue shift due to nonplanarity is apparent in the spectrum of 2,3-di-*t*-butylbutadiene,[23] a molecule which is extremely nonplanar for steric reasons, and which consequently has its $N \rightarrow V_1$ band at 1860 Å.

Concluding Remarks

We have shown how photoelectron spectroscopy in this instance can be used to give quick, easily interpretable information about the crude molecular structure of a molecule and have supported the interpretation by an optical study which yielded a very approximate value for the dihedral angle of C_4F_6. There are of course much more accurate, but also more tedious techniques available for revealing structure. In an attempt to confirm or refute the centrosymmetric structure of 1,1,4,4-tetrafluorobutadiene, Beaudet[5] made a careful search for microwave absorption in this molecule. Because such an absorption is forbidden in a nonplanar centrosymmetric molecule, but otherwise allowed, the fact that no absorption was found led him to conclude that the molecule was nonpolar and therefore centrosymmetric. At our request, Professor Laurie[24] has performed this experiment in the same spirit using hexafluorobutadiene and reports that a most extensive and complicated spectrum was readily observed. Pending detailed analysis of the spectrum, one can only say that this is to be expected for the noncentrosymmetric molecule postulated here. Electron diffraction studies provide accurate molecular parameters and, as it happens, the electron diffraction data had been recorded[25] before our work described here, but Andreassen, *et al.*,[25] had been unable to fit it to any structure (the carbon–fluorine bond length is similar to the carbon–carbon length). They had, however, not tried a cisoid conformation. Following our suggestion of a cisoid structure, they were able to complete the analysis of the data, which yielded a value of 47.60 ± 0.58° for the dihedral angle. The rather good agreement of our rough value with this figure must be considered somewhat fortuitous.

The answer to the question of why hexafluorobutadiene assumes the *cis*-bent geometry is no less subtle than that to the question of conformation in ethane. That hexafluorobutadiene should be bent, whereas butadiene and 1,1,4,4-tetrafluorobutadiene are planar is clear enough from molecular models, which show a very disadvantageous overlap of orbitals between fluorine atoms on C_1 and C_3, and on C_2 and C_4 in the planar configuration. As regards a *cis*-bent *vs.* a

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(21) N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, 86, 2811 (1964).

(22) G. Belanger and C. Sandorfy, *Chem. Phys. Lett.*, 3, 661 (1969).

(23) H. Wynberg, A. de Groot, and D. W. Davies, *Tetrahedron Lett.*, 1083 (1963).

(24) V. W. Laurie, private communication.

(25) A. Andreassen, C. H. Chang, and S. H. Bauer, private communication.

trans-bent configuration, we point out that the former has a less repulsive alignment of the $F_2C{=}CF$ group dipole moments than does the latter. However, the final answer to this question is bound to be much more complicated.

Acknowledgments. It is a pleasure to thank Dr. S. L. Manatt for a sample of 1,1,4,4-tetrafluorobutadiene, and Mr. N. A. Kuebler for running the optical spectra for us. Additionally, discussions with Professor V. W. Laurie and Dr. A. Andreassen are acknowledged with thanks.

Ground States of Conjugated Molecules. XXII. Polarographic Reduction Potentials of Hydrocarbons[1]

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Abstract: The polarographic reduction potentials of 76 aromatic hydrocarbons correlate well with electron affinities calculated by a recently described semiempirical SCF MO procedure. Points of attachment of the first two hydrogen atoms are predicted; in the few cases where data are available they confirm the predictions. The available values for polarographic oxidation potentials correlate well with calculated ionization potentials.

Correlations between the polarographic reduction half-wave potentials ($-E_{1/2}$) of conjugated hydrocarbons and the lowest unoccupied HMO orbital energies ($-m_{n+1}$) have been described by many authors,[3-7] giving in all cases reasonably good correlations with experiment, and some analogous correlations have also been reported using the Pariser-Parr method.[8] Here we present a correlation between the polarographic reduction half-wave potentials and electron affinities calculated by the variable-β SCF MO method recently developed in this laboratory.[9-12] We have also used this procedure to calculate the points of attachment of the first two hydrogen atoms during reduction by electron transfer, and finally, the available data concerning polarographic oxidation potentials have been correlated with calculated ionization potentials.

Theoretical Method

Reduction of an aromatic hydrocarbon (R) by a reversible one-electron transfer leads to the radical anion (R^-)

$$R + e \rightleftharpoons R^- \qquad (1)$$

The free energy change ($\Delta F°$) for the above process in solution is as follows

$$\Delta F° = (F°_{R})_{\text{gas}} - (F°_{R^-})_{\text{gas}} + (F°_{\text{electron}})_{\text{Hg}} + (\Delta F°)_{\text{solv}} \qquad (2)$$

The difference $(F°_{R})_{\text{gas}} - (F°_{R^-})_{\text{gas}}$ is equal to the electron affinity (A) of the molecule R in the gas phase, if we neglect entropy effects.

On the other hand, one can write down the half-wave potential ($E_{1/2}^{\text{red}}$) for a reversible one-electron electrode process as follows

$$-E_{1/2}^{\text{red}} = \frac{\Delta F°}{\mathfrak{F}} - \frac{RT}{\mathfrak{F}} \ln \left(\frac{D_R}{D_{R^-}}\right)^{1/2} + \frac{RT}{\mathfrak{F}} \ln \frac{F_R}{F_{R^-}} \qquad (3)$$

where $\mathfrak{F}$ is the Faraday constant, R is the gas constant, T is temperature in degrees Kelvin, and D_R and D_{R^-} and F_R and F_{R^-}, are, respectively, the diffusion coefficients and activity coefficients of R and R^-. Since these should be very similar, terms involving them may reasonably be neglected; *e.g.*, (3) then becomes

$$-E_{1/2}^{\text{red}} = \frac{\Delta F°}{\mathfrak{F}} \qquad (4)$$

Substituting A into eq 2 using eq 4

$$-E_{1/2}^{\text{red}}\ \frac{1}{\mathfrak{F}}[A + (F°_{\text{electron}})_{\text{Hg}} + (\Delta F°)_{\text{solv}}] \qquad (5)$$

The last two terms in eq 5, for polarographic reduction of a series of similar compounds under similar experimental conditions, should be constant. In this case

$$-E_{1/2}^{\text{red}} = \frac{A}{\mathfrak{F}} + \text{constant} \qquad (6)$$

A plot of $-E^{1}/_{2}^{\text{red}}$ *vs.* A should then be linear.

A similar relationship should hold between the polarographic oxidation potentials of hydrocarbons ($E_{1/2}^{\text{ox}}$) and calculated ionization potentials (I); *i.e.*

$$E_{1/2}^{\text{ox}} = I + \text{constant} \qquad (7)$$

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[3] A. Maccoll, *Nature (London)*, **163**, 178 (1948).

[4] L. E. Lyons, *ibid.*, **166**, 193 (1950).

[5] A. Pullman, B. Pullman, and G. Berthier, *Bull. Soc. Chim. Fr.*, 591 (1950).

[6] G. J. Hoijtink and J. van Schooten, *Recl. Trav. Chim. Pays-Bas*, **71**, 1089 (1952).

[7] G. J. Hoijtink, *ibid.*, **75**, 1525 (1955).

[8] J. Koutecký, *Z. Phys. Chem. (Frankfurt am Main)*, **52**, 8 (1967).

[9] A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965).

[10] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965).

[11] M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969).

[12] M. J. S. Dewar and T. Morita, *ibid.*, **91**, 796 (1969).