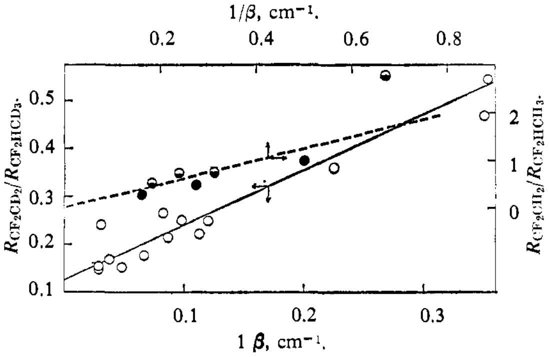

Figure 5. Plot of $R_{\text{elimination}}/R_{\text{stabilization}}$ *vs.* $1/\beta$ (see Figure 2): ○, $R_{CF_2=CD_2}/R_{CF_2HCD_3}$ at 240°; ● and ◒, $R_{CF_2=CH_2}/R_{CF_2HCH_3}$ at 145 and 188°, respectively.

The evidence that we have presented strongly suggests that the "hot" molecule CF_2HCD_3* may decompose by two, and probably three, competing unimolecular processes.[24] A complete understanding of this complex nonequilibrium system will further depend upon an analysis of the isotope effects.

Acknowledgments. We thank the referees for helpful comments when some of these data were submitted in preliminary form, and Professors F. S. Rowland and D. W. Setser for prepublication copies of their manuscripts.

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(24) A referee has observed that the disproportionation between any radical (CF_2H, CD_3, CD_2COCD_3, CF_2COCF_2H) in the system and CF_2H will yield CF_2 and that the reaction sequence

$$CF_2 + CD_2COCD_3 \longrightarrow (CF_2CD_2COCD_3)^* \longrightarrow CF_2CD_2 + COCD_3$$

accounts for the CF_2CD_2. We make the following points.

(a) Probably only the self-disproportionation *vs.* recombination of CF_2H's (k_d/k_r) is important, and is equal to 0.19;[6] values of k_d/k_r (to give CF_2) are for $CFH_2 + CF_2H = 0.06$,[6] for $CF_3 + CF_2H = 0.09$ (M. J. Perona and G. O. Pritchard, to be published), and for $CH_3 + CF_2H = 0$.[18a] The fate of the CF_2 has been difficult to establish unequivocally,[6] but fluoropropanes, from combination with monoradicals, have recently been observed (M. G. Bellas, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, 43, 1022 (1965); J. B. Hynes, R. C. Price, W. S. Brey, Jr., M. J. Perona, and G. O. Pritchard, *ibid.*, **45**, 2278 (1967); and to be published).

(b) A pathway involving CF_2 cannot be ruled out, and, where we conducted analysis for $C_2F_4H_2$, we find that $0.19C_2F_4H_2 > CF_2CD_2$. Similarly $0.19C_2F_4H_2 > CF_2CH_2$.[18a] However, the participation of acetonyl radicals cannot be assumed under all of our reaction conditions, although CF_2CD_2 is formed under all conditions. In our previous low-pressure experiments,[6] abstraction from the fluoroacetones was negligible up to 500°K, and the Arrhenius parameters are similar to those for d_6-acetone (with CD_3 or CF_2H), with $E^* = 10$–13 kcal mole^{-1}. At higher pressures abstraction is to be expected but not at room temperature; note the CF_2CD_2 production in Table I for the run at 298°K.

(c) Conversely, the decomposition of $(CF_2CD_2COCD_3)^*$ will not be favored at higher pressures.

Electronic States of Perimeter π Systems. IV.[1a] The Electronic Spectrum of [18]Annulene

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Contribution from Laboratorium für organische Chemie, Eidg. Technische Hochschule, Zürich, Switzerland, and Physikalisch-chemisches Institut der Universität Zürich, Zürich, Switzerland. *Received March 7, 1968.*

Abstract: It is shown that the electronic spectra of [18]annulene (VI) recorded so far have been incomplete and that there is a long-wave transition $B_{2u} \leftarrow A_{1g}$ ($^1L_b \leftarrow {}^1A$) at 13,000 cm^{-1}. This is in perfect agreement with theoretical predictions.

Recent experimental and theoretical investigations of the bridged [*n*]annulenes I,[2] II,[3] or III[4] (where $n = 2 + 4r$ satisfies the Hückel rule for closed-shell π perimeters) have shown that "aromatic" π-electron delocalization is not hampered noticeably even by the lack of coplanarity found for the peripheral π systems of I and II.[5] This conclusion is also supported by nmr and esr data.[6] In particular, the positions, intensities, and directions of polarization of the absorption bands in the electronic spectra of these compounds do not differ seriously from those predicted for the corresponding fully symmetrical all-*cis* models IV and V of D_{nh} symmetry by the standard many-electron treatments, *e.g.*, the Pariser–Parr–Pople (PPP) configuration interaction procedure.[7] This is shown in Table I, where the experimental data are compared with the results obtained from a PPP model of the type proposed by Longuet-Higgins and Salem.[8]

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(1) (a) Part III: W. Grimme, E. Heilbronner, G. Hohlneicher, E. Vogel, and J.-P. Weber, *Helv. Chim Acta*, **51**, 225 (1968). (b) Eidg. Technische Hochschule. (c) Universität Zürich.

(2) H.-R. Blattmann, W. A. Böll, E. Heilbronner, G. Hohlneicher, E. Vogel, and J.-P. Weber, *Helv. Chim. Acta*, **49**, 2017 (1966).

(3) E. Heilbronner, H. Labhart, Z. Silberman, E. Vogel, and J.-P. Weber, in preparation.

(4) H.-R. Blattmann, V. Boekelheide, E. Heilbronner, and J.-P. Weber, *Helv. Chim. Acta*, 50, 68 (1967).

(5) I(CH_2): M. Dobler and J. D. Dunitz, *ibid.*, **48**, 1429 (1965); I(O): N. A. Bailey and R. Mason, *Chem. Commun.*, 1039 (1967); II(O): P. Ganis and J. D. Dunitz, *Helv. Chim. Acta*, 50, 2369 (1967). The π perimeter in III is planar: A. W. Hanson, *Acta Cryst.*, **18**, 599 (1965).

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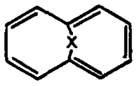
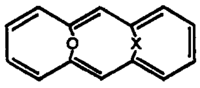
(7) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); R. Pariser *ibid.*, **24**, 250 (1956); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953), *Proc. Phys. Soc.* (London), **A68**, 81 (1955).

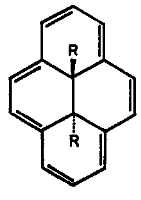
(8) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (London), **A251**, 172 (1959); **A255**, 435 (1960); **A257**, 445 (1960).



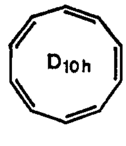
I(X)
X = CH_2, O,
NH,NCH_3



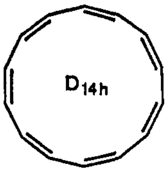
II(X)
X = CH_3, O



III(R)
R = CH_3, CH_2CH_3



IV



V

Table I. Electronic Spectra of Benzene, Bridged [10]- and [14]Annulenes, and [18]Annulene[a]

	β	γ_{11}	γ_{12}
Model A[b]	−18,040 cm^{-1}	64,500 cm^{-1}	11,500 cm^{-1}
Model B[c]	−2.5 eV	7.0 eV	1.7 eV
	−20,200 cm^{-1}	56,500 cm^{-1}	13,700 cm^{-1}

n	Compound	$^1L_b \leftarrow {}^1A$ $(B_{2u})^e$	$^1L_a \leftarrow {}^1A$ $(B_{1u})^e$	$^1B_{a,b} \leftarrow {}^1A^d$ $(E_{1u})^e$	Ref
6	Benzene	40	49	54	
	Model A	38	48	54	
	Model B	43	48	59	
10	I(CH_2)	28	34	39	2
	I(O)	25	34	39	2
	I(NH)	25	32	37	2
	I(NCH_3)	27	34	40	2
	IV, Model A	23	30	35	
	Model B	25	30	38	
14	II(CH_2)	19	24	31	3
	II(O)	18	24	31	3
	III(CH_3)	16	21	28	4
	III(CH_2CH_3)	15	21	28	4
	V, Model A	16	22	25	
	Model B	18	22	27	
18	VI	13	22	27	
	Model A	13	17	20	
	Model B	14	17	22	

[a] Band positions $\tilde{\nu}$ are given in kK = 10^3 cm^{-1}. (For definition of theoretical models A and B, see text.) [b] E. Heilbronner and J. N. Murrell, *Mol. Phys.*, **6**, 1 (1963). [c] E. Weltin, J.-P. Weber, and E. Heilbronner, *Theoret. Chim. Acta*, **2**, 114 (1964). [d] Center of gravity (estimated) for the ^1B_a and ^1B_b bands. [e] Irreducible representation for the corresponding π perimeter of D_{nh} symmetry.

From such a model it follows that the three lowest electronically excited states belong to the following irreducible representations of the group D_{nh}

Irreducible representation	(A_{1g})	B_{2u}	B_{1u}	E_{1u}
Platt symbol	(^1A)	^1L_b	^1L_a	$^1B_{a,b}$

$$\xrightarrow[\text{increasing energy}]{}$$

The reduction in symmetry from D_{nh} to that of the compounds I (C_{2v}), II (C_{2v} or C_s), and III (C_{2h}), the bridging groups in I and II, or the central R-C-C-R unit in III do not change the general characteristics expected for the fully symmetrical D_{nh} systems in a fundamental way.[2-4] The even perimeters in I, II, and III are alternant π systems,[9] so that inductive effects exert only second-order perturbations on the band positions.[10] A more pronounced effect can be ascribed to homoconjugation between the bridged centers (1,6 in I and 1,6; 8,14 in II[1a,2]) which leads to appreciable mixing of configurations and which is in part responsible for the observed splitting of the $^1B_{a,b}$ state. The influence of the breakdown of σ-π orthogonality in I and II is difficult to assess, and the same is true for the novel type of hyperconjugation associated with the two axial methyl groups in III. However, semiempirical treatments of all such perturbations seem to indicate that they will result only in small, albeit significant, shifts of the bands and thus will not affect the arguments presented in this paper.

This is reflected in the values given in Table I, where it is shown that the position of the ^1L_b and ^1L_a band, and the center of the ^1B_a, ^1B_b bands, is limited to a small wave-number range for a given value n of centers in the perimeter.

The simplest many-electron model which incorporates the minimum number of parameters necessary to obtain a semiquantitatively correct picture of the observed sequence of states is that proposed by Dewar and Longuet-Higgins.[11] It has been subsequently applied to cyclic polyenes by Longuet-Higgins and Salem.[8] In this model, which is fully described by Pople,[12] one defines the ground state

$$\Gamma = \| 0\,\bar{0}\,1\,\bar{1}\,-1\,-\bar{1}\cdots r\,\bar{r}\,-r\,-\bar{r} \|$$

of the D_{nh} model in terms of molecular orbitals

$$\psi_j = \frac{1}{\sqrt{n}} \sum_{\mu=0}^{n-1} \left(\exp\frac{2\pi i}{n} j\mu\right)\phi_\mu$$

which are occupied by pairs of electrons up to and including the degenerate orbitals ψ_r and ψ_{-r}, with $r = (n-2)/4$. The four monoexcited singlet configurations $\chi_r^{\,r+1}$, $\chi_r^{\,-(r+1)}$, $\chi_{-r}^{\,-(r+1)}$, and $\chi_{-r}^{\,r+1}$, *e.g.*

$$\chi_r^{\,r+1} = \frac{1}{\sqrt{2}}\{\|0\,\bar{0}\cdots r\,\overline{r+1}\,-r\,\overline{-r}\| +$$
$$\|0\,\bar{0}\cdots r+1\,\bar{r}\,-r\,\overline{-r}\|\}$$

interact under the influence of a many-electron Hamiltonian to yield the following descriptions for the three lowest singlet states of a D_{nh} perimeter.

$$\left.\begin{aligned}\Psi_4(^1B) &= \frac{1}{\sqrt{2}}(\chi_r^{\,r+1} + \chi_{-r}^{\,-(r+1)})\\ \Psi_3(^1B) &= \frac{1}{\sqrt{2}}(\chi_r^{\,r+1} - \chi_{-r}^{\,-(r+1)})\end{aligned}\right\} E_{1u}$$

$$\Psi_2(^1L_a) = \frac{1}{\sqrt{2}}(\chi_r^{\,-(r+1)} + \chi_{-r}^{\,r+1}) \quad B_{1u}$$

$$\Psi_1(^1L_b) = \frac{1}{\sqrt{2}}(\chi_r^{\,-(r+1)} - \chi_{-r}^{\,r+1}) \quad B_{2u}$$

Calculation of the excitation energies $\epsilon(^1B_{2u}) - \epsilon(^1A_{1g})$, $\epsilon(^1B_{1u}) - \epsilon(^1A_{1g})$, $\epsilon(^1E_{1u}) - \epsilon(^1A_{1g})$ using only the resonance integral β and the two-center repulsion integrals γ_{11} and γ_{12} as parameters[8,13] shows that they

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(9) C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940).

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(12) J. A. Pople, *ibid.*, **A68**, 81 (1955).

(13) E. Heilbronner and J. N. Murrell, *Mol. Phys.*, **6**, 1 (1963).

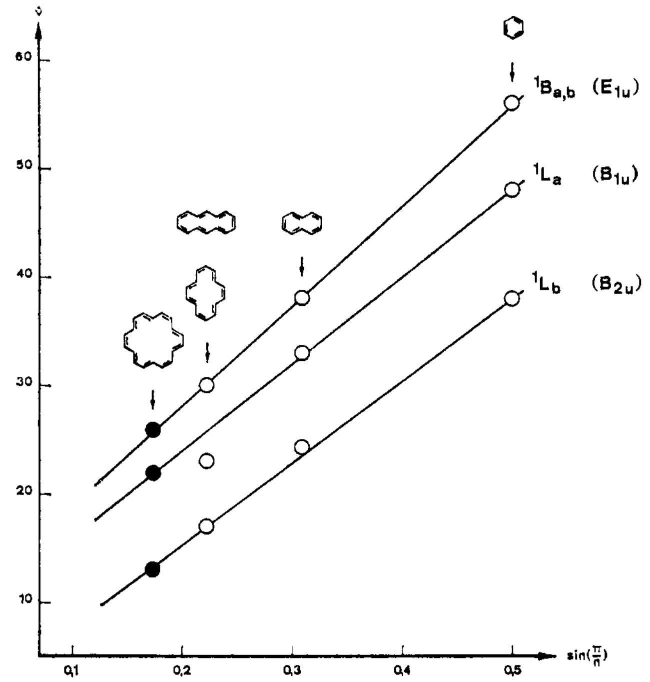
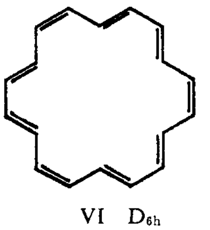


Figure 1. Dependence of band position $\tilde{\nu}$ on the parameter $\sin(\pi/n)$: Open circles, mean values for the band positions given in Table I (only the perimeter π system of the compounds I, II, and III is indicated); full circles, observed values for [18]annulene (see Table III and Figure 2). The irreducible representations refer to the corresponding π perimeters of symmetry D_{nh}.

are to a first approximation linear functions of $\sin(\pi/n)$. Therefore, one expects that the observed band positions $\tilde{\nu}$, as given in Table I, will yield a reasonably linear relationship if plotted against $\sin(\pi/n)$. This is shown in Figure 1, where the mean values of the wave numbers $\tilde{\nu}$ quoted for each set of compounds with given n and for a given type of band have been used (open circles). Even though the perimeter π systems in I, II, and III deviate appreciably from a D_{nh} symmetry and must contain perturbations due to the bridging groups, the expected relationship is well satisfied.

Even if we dismiss for the moment the theoretical basis on which Figure 1 was constructed and if we regard the $\tilde{\nu}$ *vs.* $\sin(\pi/n)$ plot only as an empirical relationship, then we obtain from it the following predictions for n = 18, *i.e.*, for the band positions in the electronic spectrum of [18]annulene (VI).[14]



VI D_{6h}

$$\left.\begin{array}{l} \tilde{\nu}(^1B_{2u}) \approx 13{,}000\ \text{cm}^{-1} \\ \tilde{\nu}(^1B_{1u}) \approx 20{,}000\ \text{cm}^{-1} \\ \tilde{\nu}(^1E_{1u}) \approx 26{,}000\ \text{cm}^{-1} \end{array}\right\}\ \text{estimated from Figure 1}$$

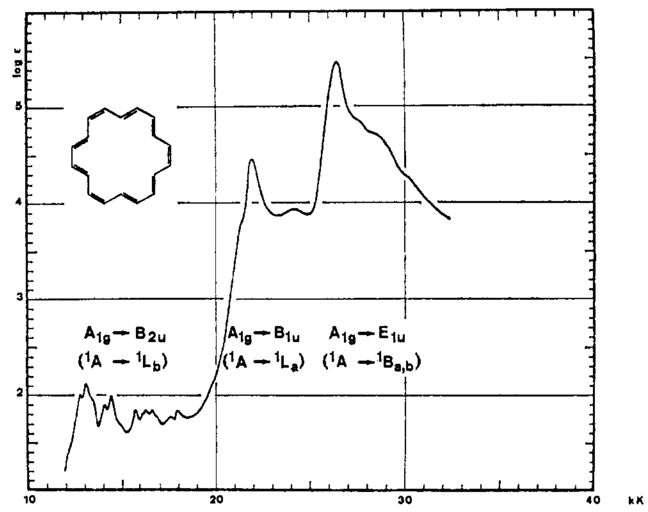


Figure 2. Electronic spectrum of [18]annulene (solvent, benzene).

For obvious reasons these are practically the values predicted from the theoretical model quoted above (see Table I) and also those which have been obtained by more sophisticated computations (based on the known geometry of VI[15] as shown in Table II). This result was in sharp contrast with the experimental determinations reported so far,[8,16–18] which located the long-wave absorption edge of the spectrum near 20,000 cm^{-1} and the first maximum at 22,000 cm^{-1}. On the other hand, the first transition is predicted by theory to be not only symmetry forbidden ($^1B_{2u} \leftarrow {}^1A_{1g}$) but also forbidden in view of the vanishing transition density: $\Gamma \cdot \Psi_1(^1B_{2u}) = 0$ in the usual zero differential overlap approximation.[8,16] The corresponding band must necessarily be extremely weak, and it seemed therefore quite probable that it had simply escaped observation because of inadequate recording conditions.

Table II. Theoretical Predictions for the Band Locations in the Electronic Spectrum of [18]Annulene[a]

	$^1L_b \leftarrow {}^1A$ (B_{2u})	$^1L_a \leftarrow {}^1A$ (B_{1u})	$^1B_{a,b} \leftarrow {}^1A$ (E_{1u})	Ref
Moffitt	13.70	17.24	19.61	*d*
Longuet-Higgins and Salem	12.23	17.10	19.40	8
Pariser and Parr	13.23	16.80	33.92	16
Weiss and Gouterman	12.16[b]	16.28	17.56	*e*
	11.48[c]	17.62	26.49	

[a] Values in kK = 10^3 cm^{-1}. [b] Only singly excited configurations. [c] Singly and doubly excited configurations. [d] W. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954). [e] C. Weiss, Jr., and M. Gouterman, *ibid.*, **43**, 1838 (1965).

As shown in Figure 2 and in Table III, this is indeed the case. The long-wave onset of the spectrum is found at 13,000 cm^{-1} in perfect agreement with both the extrapolated value (see Figure 1) and that predicted by theory (see Table I). Its fine structure is that expected for a $^1B_{2u}$ band which gains its intensity through vibronic interactions. Insertion of the observed values for the band positions into Figure 1 (full circles) yields a very satisfactory straight-line relationship.

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(16) M. Gouterman and G. Wagnière, *J. Chem. Phys.*, **36**, 1188 (1962).

(17) B. Briat, D. A. Schooley, R. Records, E. Bunnenberg, and C. Djerassi, *J. Am. Chem. Soc.*, **89**, 7062 (1967).

(18) F. Sondheimer, private communication.

Table III. Characteristic Values of the Electronic Spectrum of [18]Annulene (VI)[a]

	Chloroform as solvent				Benzene as solvent			
Band	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ΔE, eV	Log ϵ	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ΔE, eV	Log ϵ
	(815)	(12.3)	1.52	1.70	(810)	(12.3)	1.52	1.50
	(799)	(12.5)	1.55	1.95	779	12.8	1.59	2.00
	785	12.7	1.58	2.05	764	13.1	1.62	2.10
B_{2u}	768	13.0	1.61	2.15	(752)	(13.3)	1.65	1.90
	755	13.2	1.64	2.00	708	14.1	1.75	1.90
	722	13.8	1.71	2.00	692	14.4	1.78	2.00
	712	14.0	1.74	2.05	(675)	(14.8)	1.84	1.70
	694	14.4	1.79	2.15	636	15.7	1.95	1.85
	680	14.7	1.82	2.00	(622)	(16.1)	2.00	1.80
	660	15.2	1.88	1.95	616	16.2	2.01	1.85
^1L_b	638	15.7	1.95	2.10	603	16.6	2.06	1.85
	628	15.9	1.97	2.10	(595)	(16.8)	2.08	1.80
	606	16.5	2.05	2.15	569	17.6	2.18	1.80
	(580)	(17.2)	2.13	2.15	559	17.9	2.22	1.85
	571	17.5	2.17	2.25				
	561	17.8	2.20	2.30				
B_{1u}	(467)	(21.4)	2.65	3.80	(465)	(21.5)	2.67	3.90
	456	21.9	2.72	4.45[b]	456	21.9	2.72	4.45[b]
^1L_a	429	23.3	2.89	3.85				
	414	24.2	3.00	3.95[b]	412	24.3	3.01	3.95[b]
E_{1u}	378	26.5	3.29	5.50[b]	379	26.4	3.27	5.50[b]
	(365)	(27.4)	3.40	5.00	(365)	(27.4)	3.40	4.90
	(350)	(28.6)	3.55	3.80	(350)	(28.6)	3.55	4.70
$^1B_{a,b}$					(335)	(29.9)	3.70	4.30

[a] Values in brackets refer to shoulders. The log ϵ values have been calibrated on the values given by Sondheimer, *et al.*,[14] for the maxima at 456, 414, and 378 nm. Wave numbers $\bar{\nu}$ are given in kK = 10^3 cm^{-1}. [b] Calibration intensities, ref 23.

The results summarized in Figure 2 and in Table III confirm what had been already suspected by Longuet-Higgins and Salem,[8,19] namely that the strong band at 20,000 cm^{-1} in the spectrum of VI is the ^1L_a (B_{1u}) and not the ^1L_b (B_{2u}) band of [18]annulene. The good agreement with theory, as far as the relative sequence and the intensity relationship of the bands are concerned, as well as the vibrational fine structure of both the B_{1u} band (incorrectly identified as a superposition of B_{1u} and B_{2u} in ref 16) and the newly discovered B_{2u} band seem to indicate that contrary to previous assumptions[8,20,21] there is no need to postulate bond alternation in the ground state and/or in the electronically excited state of VI. This would also be in agreement with the results of a reexamination of the theory of bond alternation in annulenes and other nonsaturated hydrocarbons.[22] However, we believe that the relative positions of the B_{2u}, B_{1u}, and E_{1u} bands can only be explained if bond alternation (at least in the ground state) is postulated.

A detailed analysis of this problem and of the vibrational pattern of the B_{2u} band will be published elsewhere.

Experimental Section

The electronic spectrum of VI was recorded in chloroform and in benzene from two independent samples (one provided by Professor F. Sondheimer, the other by Dr. R. Wolovsky) on a Cary 14 spectrophotometer (concentration $\sim 10^{-3}$ *M*, cell length 1 cm, 0.1 optical density slide wire). The sample provided by Dr. R. Wolovsky was a hexadeuterio derivative of VI. However, no significant difference was found at the resolution used in this work, even for the fine structure of the B_{2u} (L_b) band. The spectrum agrees with those published previously[8,14] except for the new band at 13,000 cm^{-1}. In the spectrum recorded by Sondheimer, *et al.*,[14] in benzene, there is a small additional maximum at 23,000 cm^{-1} (missing in the spectrum of Figure 2) which, according to a private communication by Professor Sondheimer, might be due to an instrumental error. The solutions of VI are sensitive to light and the optical density decreased by about 8% during the 10 min it took to record that part of the spectrum which lies between 600 and 1000 nm. This is due to the fact that in a Cary 14 spectrometer the sample is exposed to the full intensity of the light source for recordings in the above-mentioned range. The relative decrease is the same for all bands in the spectrum. The extinction coefficients of the long-wave B_{2u} band given in Figure 2 and Table III have been extrapolated to time zero and are therefore corrected for the photoreaction of the compound.

Acknowledgments. We thank Professor F. Sondheimer for his interest and for a stimulating correspondence. He and Dr. R. Wolovsky provided the samples of [18]annulene used in this investigation. Their generous help is gratefully acknowledged. This work was supported by the Schweizerische Nationalfonds (Project No. 4651) and by the J. R. Geigy AG., Basel.

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(19) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, p 369.

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(21) Y. Ooshika, *J. Phys. Soc. Japan*, **12**, 1238, 1246 (1957).

(22) G. Binsch, E. Heilbronner, and J. N. Murrell, *Mol. Phys.*, **11**, 305 (1966); G. Binsch and E. Heilbronner, submitted for publication.