Vapor Phase Chromatography.—Gas chromatography was carried out using a standard Perkin–Elmer vapor fractometer model 154 B equipped with a $^1/_4'' \times 6'$ aluminum column packed with 0.5% polyethylene glycol 400 on glass beads. Helium was used as carrier gas, flowing at a rate of 50 cc. per minute. The results are tabulated below. The resolution in the cases of epimeric pairs of compounds was quite good.

Compound	Column temp., °C.	Retention time, min.	Purity
Ia	112	2.90	>99.5%
Ib	112	3.75	>99.5%
Ic	125	6.00	No detectable impurity
Id	125	6.65	No detectable impurity
XII	143	3.00	No detectable impurity

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Neighboring Carbon and Hydrogen. XXXIV. Interaction of Non-conjugated Chromophores[1]

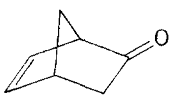
BY C. F. WILCOX, JR.,[2] S. WINSTEIN AND W. G. McMILLAN

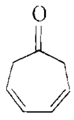
RECEIVED AUGUST 3, 1959

Three of the common semi-empirical wave-mechanical methods have been applied to the problem of interaction of non-conjugated chromophores in bicycloheptadiene and bicyclooctatriene. The simple LCAO model, as well as the more refined models of Pariser and Parr and Longuet-Higgins, agree in describing the ground state of bicycloheptadiene as the classical Kekulé structure, the predicted delocalization energy being zero. Similarly, bicyclooctatriene is predicted to have no homoconjugative stabilization. Bicycloheptadiene shows ultraviolet absorption at longer wave length than does bicycloheptene, the shift being accounted for almost quantitatively by the two refined models, and only poorly by the simple LCAO model.

It is known that π-electron systems situated beta to a developing carbonium ion center can significantly influence the course and rate of reaction.[3] This anchimeric acceleration of rate has been ascribed to delocalization of the electron cloud of the neighboring π-electron substituent in the rate-determining step and calculations with the simple LCAO model lead to stabilization energies in accord with experiment and also indicate the geometrical factors leading to maximum interaction.[4]

Another somewhat analogous[3d,4] manifestation of π-electron interaction is the modification of characteristic ultraviolet absorption spectra by neighboring π-electron systems.[5] The consequences of this interaction are not readily predictable. In some cases, *e.g.*, the $n \rightarrow \pi^*$ carbonyl band of bicycloheptene-5-one (I),[6] the characteristic absorption is shifted to longer wave lengths and in other cases, *e.g.*, the carbonyl band of cyclohepta-1,3-diene-6-one (II),[7] the wave length remains unchanged and the intensity increases. A hypsochromic shift of the carbonyl band has been observed with bicycloheptene-7-one (III).[8]


I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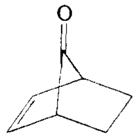
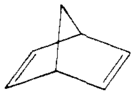
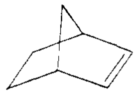

III

The alterations of the characteristic spectra of rigid bicyclic systems with non-adjacent but interacting chromophores have not received explicit theoretical treatment.[8a] In the present paper, an attempt has been made to apply three of the common semi-empirical methods to this problem of non-adjacent chromophores using bicycloheptadiene (IV) and bicycloheptene (V) as a model system. The predicted absorption spectrum of the unknown bicyclooctatriene (VI) is also presented.


IV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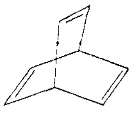
VI

Results.—In contrast with the intense ultraviolet absorption of bicycloheptene (V) at 195 mμ and butadiene at 210 mμ, bicycloheptadiene (IV) in ethanol has weak peaks at 205 mμ (ϵ 2,100), 214 mμ (ϵ 1,480), 220 mμ (ϵ 870) and a shoulder at 230 mμ (ϵ 200). These three peaks were not sharp but their definition was enhanced when the solution was cooled to 3°. In the vapor, bicycloheptadiene showed considerable fine structure (see Table I) with no less than 17 sharp bands from 226 to 199 mμ. The energy spacing of these bands was constant at 381 cm.$^{-1}$ within experimental error. There was some indication of higher energy spacing, but its definition was lost in the maze of sharply rising peaks. At wave lengths below 198 mμ the absorption increased sharply.

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[1] We are indebted to the late Martin Shatavsky for preliminary work, in 1951, on the ultraviolet and infrared spectra of bicycloheptadiene and the isolation of the 1:2 diene–silver nitrate complex from addition of diene to concentrated aqueous silver nitrate. The 1:1 complex has recently been reported by J. G. Traynham and J. R. Olechowski [THIS JOURNAL, **81**, 571 (1959)] from addition of diene to 1 *M* silver nitrate.

[2] National Science Foundation Predoctoral Fellow, 1952–1953, 1954–1955.

(3) *E.g.*, (a) S. Winstein and R. Adams, THIS JOURNAL, **70**, 838 (1948); (b) S. Winstein and A. H. Schlesinger, *ibid.*, **70**, 3528 (1948); (c) S. Winstein, H. M. Walborsky and K. C. Schreiber, *ibid.*, **72**, 5795 (1950); (d) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952); (e) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955); (f) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(4) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

(5) *E.g.*, P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950); E. A. Braude, *et al.*, *J. Chem. Soc.*, 607, 1902 (1949).

(6) P. D. Bartlett and B. E. Tate, THIS JOURNAL, **78**, 2473 (1956).

(7) J. Meinwald, S. L. Emerman, N. C. Yang and G. Büchi, *ibid.*, **77**, 4401 (1955).

(8) C. J. Norton, Ph.D. Dissertation, Harvard Univ., 1955.

(8a) NOTE ADDED IN PROOF.—A very recent exception is the paper by H. Labhart and G. Wagnière [*Helv. Chim. Acta*, **42**, 2219 (1959)] who have given a simplified treatment of β,γ-unsaturated ketones such as I.

TABLE I

ULTRAVIOLET VAPOR SPECTRUM OF BICYCLOHEPTADIENE

λ_{max}, Å.	D[a]	λ_{max}, Å.	D[a]
2258	0.155	2096	1.807
2238	.169	2080	1.790
2218	.222	2064	1.705
2199	.335	2049	1.477
2181	.699	2033	1.330
2164	1.080	2016	1.200
2146	1.295	2001	1.095
2129	1.685	1985	1.100
2113	1.885	1925[b]	>2.00

[a] Recorded optical densities, the partial pressure of bicycloheptadiene in the cell was not determined. [b] This wave length does not represent an absorption maximum, but merely the lower limit of measurement.

Preliminary Calculations.—From Schomaker's electron diffraction data for IV[9] were calculated the 2,6-C–C distance, the 2,5-C–C distance and the angle θ which is the minimum angle between the plane of the π-orbitals of one double bond and the twofold symmetry axis (see Fig. 1). These dimensions were then used to calculate overlap integrals between atoms 2 and 5 and 2 and 6 from Mulliken's tables.[10] These calculated values are included in Table II along with a summary of Schomaker's data.

Simple LCAO Method.—The first mathematical model tried was the simple LCAO model which assumes that the $(H_{ab} - S_{ab}E)$ terms for adjacent nuclei are equal to a constant β which is independent of E. This model ignores configuration interaction and specific electron repulsion. Solution of the appropriate secular equation gives rise to four nondegenerate energy levels whose energy is expressed in terms of a constant Coulomb integral and the three β's between atoms 2, 3, 5 and 6 of the diene. The β_{25} and β_{26} were expressed in terms of β_{23}, the resonance integral between atoms 2 and 3, by use of the simplified[4] Mulliken "magic formula"[11]

$$\beta' = \left(\frac{S'}{1 + S'}\right)\left(\frac{1 + S_{23}}{S_{23}}\right)\beta_{23}$$

This formula leads to values of $\beta_{25} = 0.183\ \beta_{23}$ and $\beta_{26} = 0.385\ \beta_{23}$. In terms of β_{23}, the available energy levels are

$$E - H_{22}\left\{\begin{array}{r|cl} -1.202\,\beta & \bigcirc & A_2 \\ -0.798\,\beta & \bigcirc & B_2 \\ 0\,\beta & \overline{} & \\ 0.432\,\beta & \overset{\uparrow}{\underset{\downarrow}{\bigcirc}} & B_1 \\ 1.568\,\beta & \overset{\uparrow}{\underset{\downarrow}{\bigcirc}} & A_1 \end{array}\right.$$

Calculation by Methods which Include Electron Repulsion and Configuration Interaction.—Bicycloheptadiene was also treated by the more refined semi-empirical methods of Pariser and Parr[12] and of Longuet-Higgins.[13] Both methods account for electron spin and include specific terms for electron–electron repulsions and both use antisymmetrized Slater determinants as starting wave functions. The difference between the methods lies in the choice of molecular wave functions which make up the Slater determinants. The Pariser and Parr method uses the four-center molecular orbitals obtained previously for the simple LCAO model, whereas the Longuet-Higgins method uses ethylene π-orbitals taken in various symmetry determined combinations. Application of either of these methods requires the evaluation of several new parameters—the four electron repulsion integrals, $(ii \mid jj)$, and the three resonance integrals, β_{ij} (i,j = atoms 2, 3, 5 or 6). The electron-repulsion integrals $(22|22)$ and $(22|33)$ were taken from values given by Pariser and Parr.[12] Values for $(22|55)$ and $(22|66)$ were assigned by assuming that the integrals were independent of orientation of the orbitals. The value of β_{23} was assigned by equating a Pariser and Parr solution of ethylene with the observed norbornylene transition. Values of β_{25} and β_{26} were computed from the Pariser and Parr formula for β_{ij}[14] as a function of the ij separation by treating the orbitals as having a separation equal to the equivalent distance at which two parallel atomic p-orbitals would have the same overlap integral. The selected values of these seven parameters are included in Table III.

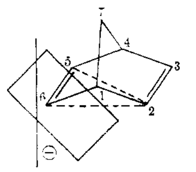

Fig. 1.—Bicycloheptadiene.

TABLE II

DIMENSIONS AND OVERLAP INTEGRALS FOR BICYCLOHEPTADIENE

Distance, Å.		Angle, °		Overlap integral	
C_{12}	1.522[a]	C_{123}	109.1[a]	S_{26}	0.083
C_{17}	1.558[a]	C_{217}	96.4[a]	S_{25}	.038
C_{23}	1.333[a]	C_{216}	102.2[a]	S_{23}	.250
C_{26}	2.369	C_{162}	38.9		
C_{25}	2.718	θ	34.6		

[a] Schomaker's data.

TABLE III

PARAMETERS FOR REFINED CALCULATIONS

Quantity	Value, e.v.	Quantity	Value, e.v.
$(22\|22)$	10.53	β_{23}	−2.40
$(22\|33)$	7.45	β_{25}	−0.008
$(22\|55)$	4.96	β_{26}	−0.075
$(22\|66)$	5.50		

The Ground State.—The simple and refined models agree in describing the ground state of bicycloheptadiene as the classical Kekulé structure IV without bonding interactions between the double bonds. The predicted delocalization energy

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(9) V. Schomaker, private communication.

(10) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(11) R. S. Mulliken, THIS JOURNAL, **72**, 4493 (1950); R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

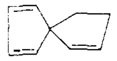
(12) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

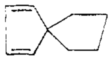
(13) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.* (*London*), **A68**, 601 (1955).

(14) R. Pariser has indicated (private communication) that their expression for $\beta(r)$ is in error and should read $\beta = -2517.5 \exp(-5.007r)$. With this correction our β_{26} would become 0.089 e.v. Either value leads to the same λ_{max} within 1 mμ.

is exactly zero. Reference to the LCAO energy levels given previously shows that this lack of delocalization energy in the ground state is independent of the choice of β_{23}, and, further, it can be shown that it is also independent of the selection of the values of β_{26} and β_{25}. In the light of this prediction, it is interesting that heats of hydrogenation give no indication of homoconjugative stabilization of bicycloheptadiene.[15]

In connection with the ground state of bicycloheptadiene, it is necessary to dispose of one possibly contradictory bit of evidence regarding the calculated and observed lack of delocalization energy. The infrared spectrum of bicycloheptadiene shows a pair of double bond stretching frequencies at 1635 (weak) and 1543 cm.$^{-1}$ (strong). This pair of frequencies is to be compared with the sole double bond stretching frequencies[16] of bicycloheptene (V) at 1568 cm.$^{-1}$ and cyclobutene at 1566 cm.$^{-1}$, which may be taken as characteristic of isolated strained double bonds. In an analogous comparison between 1,3-spiro(4,4)nonadiene (VII), which has a band at 1615 cm.$^{-1}$ (strong), and 1-spiro(4,4)nonene (VIII), which has a band at 1665 cm.$^{-1}$ (strong), Cram and Van Duuren[17] have interpreted the lowering as indicative of a conjugative effect in which the π-electrons of the double bonds interact and increase the single bond character of each function. While this conjugative effect is of importance with certain compounds, it does not seem to be the likely explanation of the shift of the strong band of either the spirononadiene VII or bicycloheptadiene (IV). A better explanation for both molecules is that a coupled oscillator phenomenon occurs[18] which splits the parent frequency into two frequencies, one of higher and one of lower frequency.


VII


VIII

Excitation Energy and Excited State.—For the simple LCAO calculation of the excitation energy of bicycloheptadiene, an appropriate value of β_{23} for spectral calculations was assigned by equating the calculated excitation energy ($2\beta_{23}$) for bicycloheptene (V) with its experimentally observed transition energy (6.33 e.v.).[19] This choice of V for reference is desirable since it partially accounts for the strain and substitution pattern of the diene. With the derived value of 3.17 e.v. for β_{23} one obtains 3.89 e.v. (318 mμ) as the lowest excitation band (B_1 to B_2 orbitals) of bicycloheptadiene. This is forbidden since the total change in π-electron symmetry is A_2. The next higher excitation band (B_1 to A_2 orbitals) is allowed.

With the more refined methods, solution of the appropriate secular determinants (including only the singly excited configurations) by either method yields a lowest energy transition of 5.78 e.v. (214 mμ). The agreement of the two refined calculations is not fortuitous. Explicit expansion of secular determinants yields identical algebraic expressions for the transition energies. This low energy transition belongs to A_2, and, hence, is forbidden. The next higher transition is allowed and is calculated to lie at 6.87 e.v. (180 mμ).

The results of the present calculations are included in Table IV along with the observed λ_{max}'s of norbornylene and bicycloheptadiene.

TABLE IV

SUMMARY OF OBSERVED AND CALCULATED λ_{max}'S

Compound	λ_{max}, mμ
Bicycloheptene (V)	195[a]
Bicycloheptadiene (IV)	211[a]
	318[b]
	214[c]

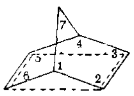
[a] Observed. [b] Calculated by simple LCAO model. [c] Calculated by either the Pariser and Parr model or the Longuet-Higgins model.

From the table it is clear that the two refined models give almost quantitative agreement with experiment in contrast to the poor fit of the simple LCAO model. This close agreement of the refined models with experiment is taken to mean that these models provide a reasonably accurate description of the π-electron interactions in bicycloheptadiene.[20]

Because of instrumental limitations, the allowed transition expected at 180 mμ on the basis of the two refined models could not be pursued below *ca.* 193 mμ. However, the rise in absorption between 199 and 193 mμ (Table I) is presumed to be due to the low-energy wing of this band.

All three of the models provide a reasonable interpretation for the observed complex series of peaks constituting the 211 mμ band. The models agree in predicting that the lowest energy transition is forbidden (and the next higher transition allowed), that the symmetry of the ground state is A_1 and that the symmetry of the excited state is A_2. The observed 381 cm.$^{-1}$ spacing of the weak 226–199 mμ band thus can probably be ascribed to either an excited state anti-symmetrical ring flapping vibration or else some combination vibration, such as a symmetrical ring flapping mixed with an anti-symmetrical stretch.

As regards the description of the excited state afforded by the different models (see IX), the simple LCAO model gives a picture of the lowest excited state which differs from that provided by the refined models. According to the LCAO model there is a half-bond in the lowest excited state between atoms 2 and 6 (also 3 and 5) and correspondingly less bonding between atoms 2 and 3



IX

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(15) R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

(16) R. C. Lord and R. W. Walker, *ibid.*, **76**, 2518 (1954).

(17) D. J. Cram and B. L. Van Duuren, *ibid.*, **77**, 3576 (1955).

(18) (a) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 199; (b) for a brief discussion and examples of coupled oscillators, see H. K. Hall, Jr., and R. Zbinden, THIS JOURNAL, **80**, 6428 (1958).

(19) S. Stokes and L. W. Pickett, *J. Chem. Phys.*, **23**, 258 (1955).

(20) It is important to note, however, that none of these models consider mixing of *s*- and *p*-orbitals. The transition energy as calculated by the refined models should not be very sensitive to admixture of *s*-character to the *p*-orbitals.

(or 5 and 6). According to the refined models which include the interactions of the more highly excited configurations, there is considerably less bonding between atoms 2 and 6. The numerical bond orders[21] are summarized in Table V.

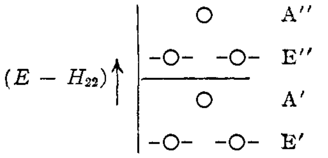
TABLE V

TOTAL BOND ORDERS IN THE LOWEST EXCITED STATE OF BICYCLOHEPTADIENE

C–C bond	LCAO model	Refined model
C_{23}	1.50	1.50
C_{26}	0.50	0.12

Calculation of Transition Energies of Bicycloöctatriene.—The general success of the calculations of λ_{max} of bicycloheptadiene lends hope that the ultraviolet spectrum of the as yet unknown bicyclooctatriene (VI) can be predicted successfully. This triene is particularly interesting, as Hine has already pointed out,[22] because it is an example of an organic molecule in which the different signs of the two lobes of the π-atomic orbitals must be taken into account when considering resonance or transition energies. Because of this difference in algebraic sign, there is no arrangement of the π-atomic orbitals which does not involve at least one antibond. It is to be expected, therefore, that the energy levels might show some rather unusual properties compared to other triolefins of lower symmetry.

If this triene is assumed to have D_{3h} symmetry (3-fold axis of symmetry and 3 vertical planes of symmetry through this axis with a horizontal plane of symmetry perpendicular to the axis), the simple LCAO method, including non-adjacent resonance integrals, leads to the sequence of energy levels



In this molecule, the lowest energy level is doubly degenerate whereas in monocyclic olefins the lowest level is always non-degenerate. A further interesting point is that if the six π-electrons are assigned to the lowest three orbitals, the π-electron energy is independent of the non-adjacent resonance integrals and is equal to $6H_{22} - 6\beta$. In other words, the delocalization energy of this triene is identically zero just as in bicycloheptadiene.

The transition energies of the triene were computed by the Pariser and Parr method assuming that the lengths of the double bonds were 1.33 Å., the lengths of the single bonds were 1.54 Å., and the carbon atoms of the double bonds were trigonally hybridized. The value of the Pariser and Parr β was taken as −2.40 e.v., the value derived from bicycloheptene and employed for bicycloheptadiene. Only singly excited local and transfer states were considered. The first few calculated transition energies are given in Table VI.

TABLE VI

CALCULATED TRANSITION ENERGIES OF BICYCLOÖCTATRIENE AND SELECTION RULES

Transition energy, e.v.	λ_{max}, mμ	Selection rule
5.77, 5.77	215	Forbidden
6.75, 6.75	184	Forbidden
6.82	182	Weakly allowed

The lowest energy degenerate transition is forbidden just as for bicycloheptadiene.[23]

Experimental Part

[2.2.1]Bicycloheptadiene-2,5 was supplied in substantial amounts by the Julius Hyman and Co., Denver, Colo., at the beginning of 1951 and also later. Pure material was obtained by fractionation through a 4-ft. column of glass helices at high reflux ratio using a nitrogen atmosphere. A large center cut, b.p. 89.0–89.1°, n^{20}_D 1.4700, was retained. On another occasion, fractionation of the diene through a 40-plate Dixon column gave rise to material, b.p. 90° (755 mm.), n^{25}_D 1.4669, d^{25}_4 0.9008, MR_D 28.38 (calcd. 29.2) [reported[22] n^{26}_D 1.4670, d^{26}_4 0.8992; also reported[24] n^{20}_D 1.4699, d^{20}_4 0.9056, MR_D 28.35].

The hydrocarbon could be kept pure for long periods by sealing it under nitrogen. Otherwise, it absorbs oxygen and undergoes change in refractive index and ultraviolet absorption spectrum. Five fractions, all with b.p. 90° (755 mm.), were sealed in the arms of a "cow" as they were collected from a fractionation of diene through a column of glass helices under a nitrogen atmosphere. The first and last fractions were opened immediately. Their n^{20}_D values were identical (1.4698). The middle fraction, kept sealed 101 days, showed the same n^{20}_D value. The ultraviolet spectra of the first and last fractions were identical within experimental error, and no difference was observed in the spectrum of fraction four, opened and measured 8 weeks later.

Fractionation of another batch of bicycloheptadiene through the 4-ft. column of glass helices gave rise to 9 fractions of diene, n^{25}_D 1.4675 ± 0.0001, sealed in ampules under nitrogen. Cooling curves were measured on a center cut in an apparatus which was checked on a sample of carbon tetrachloride, since this material melts in the proper range and its melting point has been recently reported anew.[25] For the sample of carbon tetrachloride employed, estimated to be 99.94 mole % pure, a freezing point depression of 0.11° was indicated by the difference between initial freezing point and half-frozen point. On this basis, the calculated freezing point of pure carbon tetrachloride was −22.68 ± 0.06°, compared to the recently reported value of −22.75 ± 0.03°. In the same apparatus, the bicycloheptadiene showed a freezing point depression of 0.44°, the uncorrected freezing point being −19.72° and the calculated freezing point of pure material being −19.28 ± 0.06°. From the freezing point lowering due to added *n*-heptane, a cryoscopic constant of 31.6° per mole of impurity per kg. of diene was estimated for bicycloheptadiene. On this basis, the 0.44° freezing point lowering of the bicycloheptadiene specimen corresponds to a purity of 99.87 mole %.

Silver Nitrate Complex.—The addition of bicycloheptadiene to a solution of 20 g. of silver nitrate in 25 ml. of water

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(21) C. A. Coulson, *Proc. Roy. Soc.* (*London*), **A169**, 413 (1939).

(22) J. Hine, *et al.*, THIS JOURNAL, **77**, 594 (1955).

(23) NOTE ADDED IN PROOF.—The result of an earlier and cruder calculation was communicated privately to Dr. H. E. Zimmerman and is the basis of part of the Note Added in Proof in the Communication by H. E. Zimmerman and R. M. Paufler [THIS JOURNAL, **82**, 1514 (1960)] reporting the synthesis of bicycloöctatriene (barrelene).

The new calculation described above unfortunately removes the good agreement between predicted and observed ultraviolet absorption. However, the maxima at 208 and 239 mμ reported by Zimmerman and Paufler have an average not far from the A' → E" λ_{max} = 215 mμ predicted in Table VI. This suggests that the degeneracy of E" has been split by configurational or vibrational interaction. Whether log ϵ values as large as those observed (~3) can be explained on this basis requires further consideration. In this connection we have to thank Dr. R. M. Hexter of the Mellon Institute for helpful comments.

(24) L. Schmerling, J. P. Luvisi and R. W. Welch, *ibid.*, **78**, 2819 (1956).

(25) A. K. Dunlap, *ibid.*, **77**, 2016 (1955).

produced a white precipitate. This was filtered off, washed with water, air-dried and recrystallized from 95% ethanol. Needle-like crystals were obtained which darkened on standing and burned explosively. Analysis of the compound for silver ion[26] gave a figure of 1.98 ± 0.06 moles of silver ion per mole of diene.

Ultraviolet Absorption Spectra.—The Cary recording spectrophotometer, model 11 PMS, serial 74, built by the Applied Physics Corp., Pasadena, Calif., was used to determine all of the spectra recorded down to 2000 Å. One spectrum of gas phase sample was determined down to 1900 Å. on the Cary model 14 by a representative of the company. This one spectrum agreed quantitatively with the other spectra.

The cells used in the determinations were standard Cary cells. They were flushed with dried nitrogen before being filled with a sample. Samples of diene deliberately exposed to air for half an hour showed no change in spectrum.

Spectroscopic quality *n*-heptane was prepared by shaking *n*-heptane (Phillips Petroleum Co., 99.5% pure) twice with concentrated sulfuric acid for a total of 28 hours. The *n*-heptane was then washed with 5% aqueous sodium bicarbonate and distilled water, dried over sodium sulfate, and distilled through a 35-cm. Vigreux column.

Infrared Absorption Spectrum.—The infrared absorption spectrum of the diene was determined neat with a model 21 Perkin–Elmer recording spectrophotometer using sodium chloride optics. The cell thickness was 0.03 mm. and the control settings were: resolution, 940; response, 1:1; gain, 5; speed, 10; suppression, 5. The recorded frequencies and corresponding percentage transmission were:

Frequency, cm.$^{-1}$	Transmission, %	Frequency, cm.$^{-1}$	Transmssion, %	Frequency, cm.$^{-1}$	Transmission, %
3730	92	1390	87	1016	83
3430	95	1330	59	935	52
3050	32	1310	4	910	66
2950	8	1268	79	890	54
2845	44	1229	38	874	16
1635	77	1206	42	796	28
1596	89	1150	69	721	3
1543	30	1105	85	653	16
1451	69	1061	85		

Los Angeles 24, Calif.

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[Joint Contribution from the Department of Chemistry, Fordham University, New York, N. Y., the Division of Protein Chemistry, C.S.I.R.O., Melbourne, Australia, and the Memorial University of Newfoundland, St. John's, Newfoundland]

Steric Interactions in the Absorption Spectra of 2,2'-Diaroylbiphenyls and Related Compounds. III.[1] Absorption Spectra and Structure of Benzophenones

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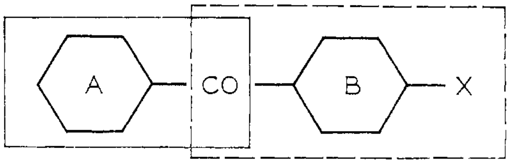
On the basis of hypotheses, postulated in previous parts of this series, substituted benzophenones may be expected to afford up to four absorption maxima (B-bands) in the region 200–360 mμ. This is, in fact, indicated by the data. The ultraviolet and infrared spectral changes on substitution are related to structural changes for a number of benzophenones on the assumption that benzophenone is initially non-planar, and that increased non-planarity may be caused by *o*-substituents.

Introduction

In previous papers of this series we have suggested the following two generalizations concerning the B-band absorptions in the ultraviolet region for 2,2'-diaroylbiphenyls, benzophenones and related compounds (for band nomenclature used, see refs.[1,3]). First, compounds of this type are assumed to absorb as partial benzenoid systems with the other benzene ring(s) exerting only a "secondary" influence on the spectra.[1] It follows from this that an unsymmetrically substituted benzophenone I may show two distinct absorption bands, one corresponding to the system –COPh involving benzene ring A, and another band corresponding to the system –COPh-*p*-X involving benzene ring B. Secondly, it was assumed[4–6] that *m*-substituted benzene derivatives may give rise to two distinct B-bands corresponding to the two monosubstituted benzene derivatives. Combining these two generalizations it follows that a *m*-disubstituted benzophenone of type II may give rise to as many as four B-bands, two involving ring A which may be associated with the partial chromophores –COPh and –PhX, and two B-bands involving ring B which may be associated with the partial chromophores –COPh and –PhY. The two –COPh absorption bands involving benzene ring A and benzene ring B are not necessarily identical because of the second-



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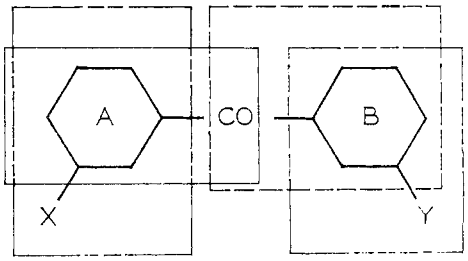

II

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