[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY]

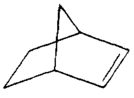
The Ultraviolet Spectrum of Bicycloheptadiene[1]

ROBERT B. HERMANN

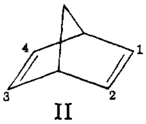
Received August 8, 1961

The ultraviolet spectrum of bicycloheptadiene was calculated by the Pariser and Parr method and the calculated $^1A_2$-$^1B_2$ splitting was found to be much larger than the experimental splitting. By giving the bridgehead carbon atom a reasonable dielectric constant, the $^1A_2$-$^1B_2$ splitting is found to be more in agreement with the experiment.

In the course of trying to determine empirically some resonance integrals at larger than nearest neighbor distances, the ultraviolet spectrum of bicycloheptadiene (II) was calculated.



I



II

Wilcox, Winstein, and McMillan (WWM)[2] have also calculated the energy of the $^1A_1 \rightarrow {}^1A_2$ forbidden transition of this compound for which the experimental value is 5.85 e.v. (211 mμ), starting with a value for β_{12} found from the norbornylene (I) 6.33 e.v. band. WWM obtained a satisfactory agreement with the experimental $^1A_1 \rightarrow {}^1A_2$ transition energy and also predicted the presence of an $^1A_1 \rightarrow {}^1B_2$ allowed transition at 6.87 e.v. (180 mμ).

A more nearly complete ultraviolet spectrum of II was obtained in the present work than was available to WWM and the position of the $^1A_1 \rightarrow {}^1B_2$ band was observed to be at 6.57 e.v. (188 mμ). A Pariser and Parr treatment was then done to find both the $^1A_2 - {}^1B_2$ splitting and the average of the two band positions. The procedure employed here differed from WWM's Pariser and Parr type treatment in several respects: (1) More configuration interaction was included in calculating the ground state, (2) the angles of the *p*-orbitals with respect to each other were taken into account in determining the electron repulsion integrals, and (3) besides the usual empirical adjustment of electron repulsion integrals originally proposed,[3] values suggested by Parr and Pariser for the spectra of ethylene-like molecules[4] were used.

The geometry of bicycloheptadiene as given by WWM was used. The value of β_{12} was used which gives the observed $N \rightarrow V$ transition in norbornylene (6.33 e.v.). All singly and doubly excited configurations were taken into account except the doubly excited configuration of symmetry $^1A_1$ which results from placing one electron in each molecular orbital. There were six configurations having symmetry $^1A_1$, two having symmetry $^1A_2$, two having symmetry $^1B_2$, and four having symmetry $^1B_1$.

In the first calculation, theoretical repulsion integrals[5] were used together with the one-center integral $(11|11) = 11.08$ e.v. The value of β between non-nearest neighbor carbon atoms was set equal to zero.

TABLE I

PARAMETERS FOR CALCULATION NO. 1

$(11\|11) = 11.08$ e.v.	$\beta_{12} = -2.70$ e.v.
$(11\|22) = 9.36$	$\beta_{13} = 0$
$(11\|33) = 5.239$	$\beta_{14} = 0$
$(11\|44) = 6.059$	

TABLE II

RESULTS OF CALCULATION NO. 1

	E (e.v.)
Lowest $^1A_1$ configuration	0.0
$^1A_1$ state after *CI*	−0.054
$^1A_1 \longrightarrow A_2$ after *CI*	5.495 (225 mμ)
$^1A_2 \longrightarrow {}^1B_2$ after *CI*	7.134 (174 mμ)
$E_{B2} \longrightarrow E'_{A2}$	1.639
Average transition energy of these two transitions	6.315
Experimental average of these two transitions	6.22
Experimental $^1A_2 - {}^1B_2$ splitting	0.73

The above calculation disagrees with experiment in two respects. First of all the calculated average of the two transition energies is 6.315 e.v. which differs from the experimental average which is 6.22 e.v. This is a consequence of using the value of β which gives the value 6.33 for the norbornylene transition. Probably with the inclusion of all higher configurations the average transition energy would approach 6.33 e.v.

The second difficulty is that the calculated $^1A_2 - {}^1B_2$ splitting is much too large even when $\beta_{23} = \beta_{14} = 0$. The expression for the splitting when $\beta_{23} = \beta_{14} = 0$ is

$$E_{B_2} - E_{A_2} = 2[K_{13} - K_{14} + (13|24) - (23|14)] \quad (1)$$

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[1] This research was supported by a grant from the American Cancer Society Institutional Research Grant.

[2] C. F. Wilcox, Jr., S. Winstein, and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

[3] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

[4] R. G. Parr and R. Pariser, *J. Chem. Phys.*, **23**, 711 (1955).

[5] C. C. J. Roothaan, "Tables of Two Center Coulomb Repulsion Integrals between 1*s*, 2*s*, and 2*p* Orbitals," Special Technical Report, Office of Naval Research (1955).

The last two terms arise from the configuration interaction matrix elements and the numbers refer here to molecular orbitals. Since K_{13} can be shown to be equal to (13|24) and K_{14} can be shown to be equal to (23|21) then

$$E_{B_2} - E_{A_2} = 4(K_{13} - K_{14}) \tag{2}$$

The difference between K_{13} and K_{14} is a function only of the difference of the repulsion integrals between atomic functions (11|33) and (11|44), and it can be shown that

$$E'_{B_2} - E'_{A_2} = 2[(11|44) - (11|33)] \tag{3}$$

The inclusion of reasonable values for β_{13} and β_{14} increases the splitting by a small amount, approximately equal to $2(\beta_{13} - \beta_{14})$ for small values of these integrals. For example, the inclusion of β as found from the Pariser and Parr formula[6] (corrected for angular dependence) increases the splitting by 0.03 e.v. In this case the corrected β's were $\beta_{14} = 0.0178$ and $\beta_{13} = 0.0031$.

In order to get better agreement with experiment one must look for a reason why the two-center atomic integrals (11|33) and (11|44) are more nearly equal than theoretically calculated. It is true that if scaled down values of these integrals are used, as originally proposed,[2] the splitting is lowered to 1.2 e.v.[7] (with $\beta_{14} = \beta_{13} = 0$) which is still too large.

If a molecular model of bicycloheptadiene is examined, it can be seen that a saturated carbon atom partially shields the p-orbital on one ethylene group from the nearest p-orbital on the second ethylene group. It will be assumed that this carbon atom, being in an sp^3 valence state and sp^3 hybridized, may be given a dielectric constant equal to that of diamond,[8] which is 5.5 when measured at a frequency of 10^8 c.p.s. (The square of the index of refraction[9] is $n^2 = 5.84$.) The dielectric constant is assumed to operate over half the spatial distance between the p-orbitals; it is also assumed to operate only in the space between the upper half of the p-orbitals; and not the lower half, and not on the space between the upper half of one 2 p-orbital and the lower half of the second 2 p-orbital, and further affect only the $2p\pi$-$2p\pi$ terms in the (11|44) repulsion integral[10] but not the $2p\sigma - 2p\pi$ or $2p\sigma = 2p\sigma$ terms. When the dielectric constants of the space between the ethylene moieties is accounted for in this manner, 5.55 e.v. is obtained for the value of (11|44). The repulsion integral (11|33), which operates essentially across a vacuum, remains unchanged. From this new value of (11|44), together with the remaining parameters in Table I, one obtains the results in Table III.

TABLE III

RESULTS OF CALCULATION NO. 2

	E (e.v.)
Lowest $^1A_1$ configuration	0
$^1A_1$ state after CI	−0.04
$^1A_1 \longrightarrow {}^1A_2$ after CI	5.982 (208 mμ)
$^1A_1 \longrightarrow {}^1B_2$ after CI	6.612 (188 mμ)
$E^1{}_{B_2} - E^1{}_{B_2}$	0.63
Average transition energy	6.297

While these results of 208 mμ for the $^1A_1 \rightarrow {}^1A_2$ transition and 188 mμ for the $^1A_1 \rightarrow {}^1B_2$ transition agree well with the experimental values 211 mμ and 188 mμ, no reliance should be placed on more than a qualitative downward adjustment of the (11|44) repulsion integrals through the use of an effective dielectric constant.

EXPERIMENTAL

A commercial grade of bicycloheptadiene was distilled from sodium and the middle fraction collected. A vapor phase spectrum was obtained from 180 mμ to 240 mμ on a Cary 14 spectrophotometer. The appearance of the spectrum was identical to that described by WWM over the range they recorded and in addition had an extinction coefficient at 188 mμ which was 1.75 times as large as that possessed by the peak at 211 mμ.

The numerical work was carried out on an IBM 650 computer with programs written based on the formulas given by R. Pariser[11] and Daudel, Lefebvre, and Moser.[12]

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(6) See ref. 3, footnote 14.

(7) Assuming the same geometry for norbornylene as for bicycloheptadiene, and using the scaled down repulsion integrals, β_{12} was evaluated from the norbornylene transition and −2.27 e.v. was obtained for this quantity. WWM has given −2.40 for β_{12}.

(8) *Handbook of Chemistry and Physics*, 39th ed., Chemical Rubber Publishing Co., 1957–1958, p. 2341.

(9) See ref. 8, p. 508.

(10) For this calculation, the electron repulsion integral is needed between the upper lobes of $2p$ atomic orbitals of carbon atoms at the distance R_{14}. This integral can be found by interpolation using values given by L. C. Snyder and R. G. Parr, *J. Chem. Phys.*, **34**, 1661 (1961).

(11) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

(12) R. Daudel, R. Lefebvre, and C. Moser, *Quantum Chemistry*, Interscience Publishers, Inc., New York, 1959, p. 471