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Dependence of the Vertical Excitation Energy of Benzene on the Size and Force Constant of the Excited State*

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Griffing[1] computed the vertical excitation energy for the first electronic transition of benzene as a function of the carbon-carbon distance (r_n) within the Sklar[2] valence bond (SVB) and Goeppert-Mayer and Sklar[3] molecular orbital (GMSMO) methods to evaluate the change on excitation of the carbon-carbon equilibrium internuclear separation (r_n^0) and of the corresponding stretching force constant, f. While ring expansion was correctly predicted, both methods appeared to predict that f increases on excitation, contrary to experiment. We shall demonstrate a) that Griffing's paradox may be resolved if terms higher than the second power in r_n are included in the energy expressions for the states and b) that a Hückel calculation leads to results qualitatively similar to those obtained from the more elaborate calculations.

If the benzene hexagon is stretched (compressed) so as to preserve symmetry, the only symmetry coordinate affected is $S = 6^{-1/2}(r_1 + r_2 + r_3 + r_4 + r_5 + r_6)$. The energy of an electronic state with respect to such distortion from its coordinate equilibrium value, S^0, can be written $E = E_0 + \frac{1}{2} f(S-S^0)^2 - g(S-S^0)^3 + h(S-S^0)^4$, where terms higher than quartic are omitted; f is the harmonic force constant. The first two derivatives of the vertical excitation energy ($\Delta E = E_e - E_g$) with respect to displacement from the ground state equilibrium value S_g^0 are then,

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$$[\partial \Delta E/\partial (S-S_g^0)]_{S=S_g^0} = f_e(S_g^0-S_e^0) - 3g_e(S_g^0-S_e^0)^2 + 4h_e(S_g^0-S_e^0)^3 , \quad (1)$$

$$[\partial^2 \Delta E/\partial (S-S_g^0)^2]_{S=S_g^0} = (f_e-f_g) - 6g_e(S_g^0-S_e^0) + 12h_e(S_g^0-S_e^0)^2 . \quad (2)$$

These equations reduce to Griffing's, with $g_e=h_e=0$. Since (vide infra) f, g, and h are positive and $f_g > f_e$, $S_e^0 > S_g^0$, the two last terms in eq. (2) have opposite sign to the first, while those in eq. (1) all have the same sign. This result suggests Griffing's paradox may arise by omission; we now proceed to evaluate the higher terms to show that $\partial^2 \Delta E/\partial (S-S_g^0)^2 > 0$.

Griffing's excitation energies have been fitted as power series in $S-S_g^0$ up to cubic terms by a least squares procedure. The derivatives are listed in Table I. These agree qualitatively with Griffing's. Table I also lists the derivatives obtained analytically in the Hückel procedure with $\beta(r_n) = \beta_0[S(r_n)/S_0]$, where β_0 is the usual Hückel β, chosen to yield the correct average excitation energy for the first excited configuration. $S(r_n)$ is the nearest-neighbor π-overlap (with Slater μ = 1.625 a.u.) and S_0 refers to the overlap at the ground state r_n^0.

The "Experimental" values in Table I were calculated with eqs. (1) and (2) employing f_e and f_g values obtained spectroscopically by Ingold et al.[4] and with their value for $(S_g^0-S_e^0)$ found by Badger's rule, which also is the value forthcoming from bond-order-bond-length relationships. "Experimental I" corresponds to $g_e=h_e=0$. Griffing's paradox is demonstrated. "Experimental II" corresponds to $h_e = 0$ and g_e obtained from a Morse potential for the symmetrical stretching coordinate. The central value is obtained with a dissociation energy D = 27 eV (corresponding to 6 carbon-carbon bonds with energies of 5.4 eV minus the excitation energy of 5 eV). This value of D gives, for a single oscillator, $\omega_e x_e = 1.06\ cm^{-1}$; the comparable spectroscopic value[5] is $\sim 0.5\ cm^{-1}$. The + and - signs respectively refer to values obtained with 13.5 eV and 54 eV for

D; this is a way of demonstrating sensitivity to $\omega_e x_e (\propto D^{-1})$. "Experimental III" was obtained as "Experimental II" with the full eqs. (1) and (2). In "Experimental IV" g_e and h_e are assigned values 0.92 and 1.27 times their previous Morse values (D = 27 eV), corresponding to $\omega_e x_e = 0.5\ cm^{-1}$. Griffing's paradox is resolved when higher order terms are included in the potentials of the states. The calculated first derivative is fairly independent of the higher order potential coefficients and the experimental values agree well with the two MO values. The experimental II, III and IV values of the second derivative are lower than those of the SVB or GMSMO methods; they are, however, quite close to the Hückel value. Upon assumption that the higher force constants are related to the harmonic one through the Morse potential, the computed derivatives together with the experimental value of f_g can alternatively be made to yield f_e and $S_g^0 - S_e^0$ through eqs. (1) and (2). One finds (with Morse D_e = 27 eV and with $h_e = 0$ for convenience) that the SVB method yields $S_g^0 - S_e^0$ and $f_e - f_g$ values respectively about twice and one-half the experimental values. The GMSMO method yields $S_g^0 - S_e^0$ close to experiment but $f_e - f_g$ nearly zero,[6] while the Hückel method yields both $S_g^0 - S_e^0$ and $f_e - f_g$ surprisingly close to experiment. $S_g^0 - S_e^0$ is not sensitive to inclusion of the higher order potential terms; this explains Griffing's ability to predict the correct order of magnitude for ring expansion upon excitation.

Table I. Expansion coefficients for vertical excitation energy as a function of symmetrical C-C displacement

Method	$-10^4 \left[\partial \Delta E/\partial (S-S_g^0)\right]$ (dyne)	$10^{-4} \left[\partial^2 \Delta E/2\partial (S-S_g^0)^2\right]$ (dyne/cm)
SVB	13.1	12.3
GMSMO	7.2	9.2
Hückel	6.5	2.6
Experimental[a] I	5.9	-5.4
Experimental[a] II	$6.6^{+0.3}_{-0.2}$	$2.3^{+3.2}_{-2.3}$
Experimental[a] III	$6.7^{+0.3}_{-0.2}$	$3.0^{+3.9}_{-2.6}$
Experimental[a] IV	6.6	2.6

[a] $S_e^0 - S_g^0 = (6)^{-1/2}\left[6(r_{n_e}^0 - r_{n_g}^0)\right]$ with $r_{n_e}^0 - r_{n_g}^0 = 0.037$ Å; $f_g, f_e = 7.61, 6.53$ mdyne/Å, following Ingold, et al., ref. 4. (A more elaborate analysis, following B. L. Crawford and F. A. Miller, J. Chem. Phys. 17, 249 (1949) leads to $f_g, f_e = 7.83, 6.81$ md/Å. Use of the latter instead of the former values would not importantly affect the results.)

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[1] V. Griffing, J. Chem. Phys. 15, 421 (1947).

[2] A. L. Sklar, Rev. Modern Phys. 14, 232 (1942).

[3] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).

[4] F. M. Garforth, C. K. Ingold, and H. G. Poole, J. Chem. Soc. 508 (1948). The numerical analysis of this paper for the "experimental" values has been used in preference to the values used by Griffing. While the force constant for symmetrical CC stretch decreases on excitation by 1.08 md/Å, that for symmetrical CH stretch increases by 0.29 md/Å. The latter effect is beyond the scope of this note.

[5] F. M. Garforth and C. K. Ingold, J. Chem. Soc. 417 (1948) and succeeding papers. They favor $\omega_e x_e \approx 0.5$ cm^{-1}. The spectroscopic $\omega_e x_e$ values refer, of course, to the normal frequency (in the presence of other excitation) while our anharmonicity refers solely to carbon-carbon stretch.

[6] G. J. Kynch and W. G. Penney, Proc. Roy. Soc. A179, 214 (1941) have carried out a thermochemically parametrized valence bond calculation which yields fair agreement with these experimental values.