

# Raman Intensity and Conjugation. 5.<sup>1</sup> A Quantitative Relationship between Raman Intensity and the Length of Conjugation and an Analysis of the Raman Intensities of Some Substituted Benzenes and Biphenyls

Eduard D. Schmid\* and Ronald D. Topsom\*

Contribution from the Institut für Physikalische Chemie, der Universität Freiburg, West Germany, and the School of Physical Sciences, La Trobe University, Bundoora, Australia 3083. Received March 7, 1980

**Abstract:** A study is reported of the Raman intensities of the  $\nu_8$  mode of benzene in a variety of conjugated hydrocarbons. It is shown that the experimental intensities can be corrected for the resonance Raman effect by using the simplified theory of Shorygin. These corrected intensities ( $S^0$ ) allow the first demonstration of a quantitative relationship between the intensity and the length  $L$ —as defined below—of a conjugated system:  $(S^0)^{1/4} = 0.241L$ . Deviation from this relationship— $[(S^0)^{1/4} - (S^0)_{\text{expt}}]^{1/4} = C_X$ —is used as a measure of deviation in conjugation relative to pure planar conjugated hydrocarbons. In sterically hindered biphenyls  $C_X$  is used as a measure of the decrease in conjugation due to twisting about the coannular (1-1') bond. In case of benzoyl derivatives  $C_X$  is related to electronic effects on conjugation. Corresponding results for substituted benzenes are shown to be broadly understandable provided that allowance is made for the length of conjugation.

The study of the mutual interaction of groups of atoms in molecules remains one of the most important problems in organic chemistry. Many physical techniques, among them infrared and nuclear magnetic resonance spectroscopy, have been usefully employed, but Raman spectroscopy has been used little. In part, this has resulted from experimental difficulties and from the ready determination of vibrational frequencies for the most important groups by infrared spectroscopy. Raman intensities are capable of providing alternative information to that obtained from infrared measurements since they depend on vibrational changes of the polarizability rather than of the dipole moments. However, as discussed below, it is difficult to correct for the resonance Raman effect and the relationship between the measured intensity and physical parameters is frequently not clear.

It has been known for some time<sup>2-4</sup> that the Raman intensities (RI) of certain molecular vibrations depend on conjugation; it has often been suggested that the RI is one of the sensitive measures of conjugation. Yet there is no well-established quantitative relationship between RI and conjugation.<sup>5-7</sup> Before proceeding further, it is necessary to be clear as to what we mean by conjugation since various authors<sup>8,9</sup> use the term in at least three different senses. First, the availability of atomic orbitals of suitable symmetry on a series of adjacent atoms leads to delocalized molecular orbitals. The greater the number of adjacent orbitals the greater the conjugation. This we refer to as the "length of conjugation". Second, the term has been used to describe the importance of such delocalization in determining particular properties such as bond lengths. Thus, while there is considerable evidence that delocalization is not of great consequence in the ground-state properties of acyclic polyenes, the system can still be described as being conjugated. Third, the term has been used to describe the extent of  $\pi$ -charge transfer between one group of atoms and another, for example, between an oxygen lone pair and the benzene  $\pi$  system in phenol. We shall refer to this as charge transfer. We refer to the total effects, insofar as they influence the Raman intensity and after allowance for the frequency dependence is made (see below), as the "conjugation effect"<sup>9</sup> (CE).

Our first interest was to investigate the dependence of RI on the length of conjugation. Earlier work has shown that the RI of the phenyl  $\nu_8$  mode changes with the angle of twist in sterically hindered biphenyls.<sup>10</sup> Thus when the rings are coplanar, the RI is at a maximum. When the rings are at right angles to each other, the RI assumes the value for two unsubstituted benzenes. The

RI of the  $\nu_8$  mode at approximately 1600  $\text{cm}^{-1}$  thus seems to provide an empirical measure of the extent of conjugation in this case. This is only valid because the resonance Raman Effect (RRE) is not of great importance.

Another example was found for the RI of diphenylpolyenes,<sup>9</sup>  $\text{C}_6\text{H}_5(\text{CHCH})_n\text{C}_6\text{H}_5$ , where both the benzene  $\nu_8$  and ethylene  $\nu_2$  modes were studied. Here the intensity appears to increase even after allowance was made for the RRE, as described below.

These results suggested that a study of conjugated hydrocarbons in which the charge transfer should be minimal might lead to a more quantitative relationship between RI and length of conjugation. The establishment of such a relationship might, in turn, allow better understanding in situations where charge transfer may also contribute to the RI.

It is important to appreciate that the theoretical background of RI is not complete and that we need to demonstrate the utility of any empirical approach employed. In particular we need to allow for the resonance Raman contribution to the overall intensity. Our results are concerned with the so-called preresonance region. We find it convenient to consider the RRE contribution through a separate frequency term. This term is quite successful in representing the observed RRE on the intensities in that part of the preresonance region where the intensity enhancement is relatively small (of the order of 1-5).<sup>9</sup> We will show that this procedure allows us to provide a quantitative description of the CE that is independent of the RRE.

**Theoretical Background.** The quantum mechanical expression for the total amount of scattered light (all polarizations, full

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(3) Shorygin, P. P. *Russ. Chem. Rev. (Engl. Transl.)* 1971, 40, 367.

(4) Jesson, F. P.; Thompson, H. W. *Proc. R. Soc. London, Ser. A* 1962, 268, 68.

(5) Pao-shan, Yü; Nikitin, N. V.; Vol'kenshtein, M. V. *Russ. J. Phys. Chem. (Engl. Transl.)* 1962, 36, 356.

(6) Shorygin, P. P.; Il'icheva, Z. F. *Izv. Akad. Nauk SSSR, Ser. Fiz.* 1958, 22, 1058.

(7) Bobrov, A. V.; Sterin, Kh. E. *Opt. Spectrosc.* 1963, 15, 68.

(8) See, for example, Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; University Press: Ithaca, New York, 1969. Dewar, M. J. S. "Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.

(9) Schmid, E. D.; Brosa, B. *J. Chem. Phys.* 1973, 58 (3), 3871.

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\* Address correspondence as follows: E.D.S., Universität Freiburg; R.D.T., La Trobe University.

Table I. Raman Data for the  $\nu_8$  Mode of Some Hydrocarbons

no.	compd	$\nu_8, \text{cm}^{-1}$	depol ratio	S	$\nu_e, \text{cm}^{-1}$	$(S^0)^{1/4}$	L, Å
1	benzene	1585/1604	0.80	0.49	49 000	0.76	2.80
2	styrene	1600	0.62	5.6	40 600	1.32	5.60
3	fulvene	1613	0.51	12.2	38 240	1.58	7.06
4	p-divinylbenzene	1609	0.53	51.3	38 850	2.19	8.40
5	PhCH=CHPh	1597	0.57	53.0 <sup>b</sup>	33 900	2.15	9.86
6	Ph(CH=CH) <sub>2</sub> Ph	1595	0.55	275.0 <sup>b</sup>	30 300	3.00	12.66
7	Ph(CH=CH) <sub>3</sub> Ph	1589/1608	0.53	950.0 <sup>b</sup>	28 250	3.82	15.46
8	Ph(CH=CH) <sub>4</sub> Ph	1582	0.52	2400.0 <sup>b</sup>	26 600	4.46	18.26

<sup>a</sup> Longest wavelength intense absorption in ultraviolet. <sup>b</sup> From ref 9.

Table II. Raman Data for the  $\nu_8$  Vibration of Monosubstituted Benzenes (PhX)

no.	X	$\nu_8, \text{cm}^{-1}$	depol ratio	$S^a$	$\nu_e, \text{cm}^{-1}$	L, Å	$(S^0)^{1/4}$ calcd	$(S^0)^{1/4}$ exptl	$\frac{(S^0)^{1/4} \text{ calcd} - (S^0)^{1/4} \text{ exptl}}{C_X}$
9	N(CH <sub>3</sub> ) <sub>2</sub>	1600	0.66	4.50	40 000	4.73	1.140	1.251	-0.111
10	NH <sub>2</sub>	1601	0.63	2.42	42 600	4.20	1.012	1.094	-0.081
11	CHO	1596	0.60	3.55	39 060	5.48	1.321	1.169	0.152
12	CN	1597	0.62	2.30	44 800	5.39	1.299	1.095	0.204
13	NO <sub>2</sub>	1589	0.70	3.10	39 700	5.44	1.311	1.137	0.174
14	OH	1595/1607	0.71	0.77	47 400	4.23	1.019	0.845	0.174
15	CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	1601	0.68	2.75	43 600	5.48	1.321	1.137	0.184
16	OCH <sub>3</sub>	1588/1603	0.76	1.06	46 200	4.76	1.147	0.909	0.238
17	Br	1577	0.76	0.97	46 500	4.63	1.116	0.891	0.225
18	Cl	1583	0.75	0.85	46 700	4.48	1.080	0.863	0.217
19	CH <sub>3</sub>	1605	0.75	0.94	48 800	3.33	0.803	0.894	-0.091
1	H	1585/1604	0.80	0.49	49 000	2.80	0.675	0.760	-0.085
20	F	1595/1603	0.74	0.56	49 300	4.13	0.995	0.787	0.208

<sup>a</sup> From ref 16. <sup>b</sup> Longest wavelength intense absorption in ultraviolet.

scattering sphere) from molecules of random orientation is given by eq 1,<sup>11</sup> where  $I_0$  is the intensity of the incident radiation of

$$I_{mn} = \text{const} N I_0 (\nu_0 - \nu_{mn})^4 \sum_{\rho, \sigma} |(\alpha_{\rho\sigma})_{mn}|^2 \quad (1)$$

frequency  $\nu_0$ ,  $N$  is the number of molecules,  $\nu_{mn}$  is the frequency shift of the scattered light, and  $(\alpha_{\rho\sigma})_{mn}$  is an element of the polarizability tensor. It is reasonable to employ the semiclassical theory of Shorygin<sup>12</sup> to our results since all the measurements were in the preresonance region. This simplification allows us to evaluate our results and, as it will be shown below, is further justified by the analysis provided. The theory is simplified by setting  $m = n$  and  $\rho = \sigma$  in the term  $(\alpha_{\rho\sigma})_{mn}$  and by neglecting damping. One obtains

$$(\alpha_{\rho\rho})_{nn} = \alpha_{\rho n} = (2/h) \sum_r [v_{rn}/(v_{rn}^2 - \nu_0^2)] |(M_\rho)_{rn}|^2 \quad (2)$$

where  $(M_\rho)_{rn}$  is the amplitude of the transition moment between vibronic states  $n$  and  $r$ . For a region sufficiently far away from resonance that damping may be neglected, then the summation over  $r$  in eq 2 may be limited to the vibronic levels of the first excited state. Taking a derivative with respect to the normal coordinate  $Q$ , one obtains eq 3, where  $\nu_e = \nu_{rn}$  is the frequency

$$\frac{\partial \alpha_{\rho n}}{\partial Q} = -(2/h) F_A |(M_\rho)_e|^2 (\partial \nu_e / \partial Q) + (2/h) F_B [\partial |(M_\rho)_e|^2 / \partial Q] \quad (3)$$

between the ground and the first excited state and  $F_A$  and  $F_B$  are frequency terms described below. Insertion into eq 1 gives the intensity within Shorygin's approximation.

A further simplification is possible if only one of the two terms in eq 3 is important. This can only be established empirically. Thus for the relative scattering coefficient,  $S$ , referred to below simply as the intensity, using exciting light polarized perpendicularly to the direction of observation, one obtains eq 4, where

$$S = \text{const} f(\nu_0, \nu_e) K \quad (4)$$

the frequency factor  $f(\nu_0, \nu_e)$  describes the deviation from the  $\nu^4$  scattering law caused by the RRE and  $K$  values<sup>9</sup> only contain molecular properties. The frequency factor can be one of the two,  $f_a (=F_A^2)$  or  $f_b (=F_B^2)$ , as given in eq 5 and 6. The more so-

$$f_a = \frac{(\nu_e^2 + \nu_0^2)^2}{(\nu_e^2 - \nu_0^2)^4} \quad (5)$$

$$f_b = \frac{\nu_e^2}{(\nu_e^2 - \nu_0^2)^2} \quad (6)$$

plicated approach of Albrecht<sup>13</sup> also follows eq 4, but allowance is made for two low excited electronic states in the frequency factor,  $f_c$ , as shown in eq 7. This reduces to eq 5 if  $\nu_e = \nu_s$ .

$$f_c = \frac{(\nu_e \nu_s + \nu_0^2)}{(\nu_e^2 - \nu_0^2)^2 (\nu_s^2 - \nu_0^2)^2} \quad (7)$$

In practice eq 4 has proved useful, and it has been found experimentally<sup>9</sup> that, for molecules of the type studied in this paper, the frequency dependence is substantially explained by the factor  $f_b$  alone. The form of the frequency independent term  $K_b$  is given in eq 8 for one direction, where the subscript zero refers to the equilibrium position.

$$K_b = [(\partial |M_e|^2 / \partial Q)_0 Q_0]^2 \quad (8)$$

Intensity variations resulting from changes in the frequency factors are usually referred to as the resonance Raman effects.<sup>3</sup> According to this arbitrary definition, the intensity changes that are not caused by variation in the frequency factor can be described as arising by changes in the CE.<sup>9</sup>

### Experimental Section

The exciting lines of krypton ion and argon ion lasers were used to investigate the frequency dependence of the vibrations. The intensity results reported in the tables are for the 4880-Å exciting line with power from 1 to 2 W. The spectra were obtained by using an apparatus previously described.<sup>14</sup> The method of calculating the relative scattering

(11) Behringer, J. *Ber. Bunsenges. Phys. Chem.* **1958**, *62*, 906.

(12) Shorygin, P. P. *Zh. Fiz. Khim.* **1947**, *21*, 1125. *Izv. Akad. Nauk SSSR, Fiz. Zemli* **1948**, *12*, 576. For a description in English of Shorygin's theory, see: Behringer, J. *Mol. Spectrosc. (Chem. Soc., London)* **1974**, *2*.

(13) Albrecht, A. C. *J. Chem. Phys.* **1961**, *34*, 1476. Albrecht, A. C., Hutley, M. C. *J. Chem. Phys.* **1971**, *55*, 4438.

(14) Schmid, E. D.; Berthold, G.; Berthold, H.; Brosa, B. *Ber. Bunsenges. Phys. Chem.* **1971**, *75*, 149.

Table III. Raman Data for the  $\nu_8$  Vibration of Substituted Biphenyls

compd	$\nu_8$ , $\text{cm}^{-1}$	$S_8^a$	$S_8^0$	$(S_8^0)^{1/4}$	$C_X$	$\theta$ , deg
benzene	1585/ 1604	0.49	0.33	0.76	0.94	(90)
2,2'-dimethyl- diphenyl	1605	1.90	1.17	1.04	0.66	72
2-methyldiphenyl	1604	3.90	2.30	1.23	0.47	59
2-phenyldiphenyl	1599	5.60	3.36	1.35	0.35	44.5
diphenyl	1593/ 1612	8.70	4.79	1.48	0.22	25
fulvene	1613	12.20	6.20	1.58	0.12	0

<sup>a</sup> From ref 10.Table IV. Raman Data for  $\nu_8$  Vibration of Benzoyl Derivatives,  $\text{C}_6\text{H}_5\text{COX}$ 

X	$\nu_8$ , $\text{cm}^{-1}$	$S_8^a$	$S_8^0$	$(S_8^0)^{1/4}$	$C_X$
$\text{NH}_2$	1602	2.18	1.036	1.009	0.312
$\text{OC}_2\text{H}_5$	1601	2.27	1.064	1.016	0.305
$\text{OCH}_3$	1602	2.30	1.078	1.019	0.302
$\text{CH}_3$	1601	2.89	1.335	1.075	0.246
$\text{CH}_2\text{Cl}$	1598	3.11	1.614	1.127	0.194
H	1596	3.55	1.865	1.169	0.152
Cl	1598	3.65	1.917	1.177	0.144
$\text{CF}_3$	1602	4.20	2.193	1.217	0.104
CN	1600	8.07	3.884	1.404	-0.083

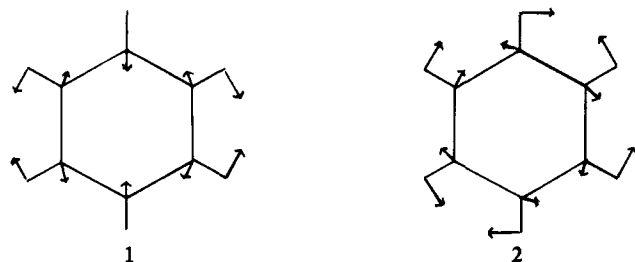
<sup>a</sup> From ref 1.

coefficients (intensities)  $S$  as defined by Bernstein and Allen<sup>15</sup> has also been reported earlier.<sup>16</sup> The error limits of the intensities are of the order of  $\pm 10\%$ . Measurements were carried out on dilute solutions in carbon tetrachloride (about  $10^{-2}$  mol  $\text{L}^{-1}$ ). The compounds studied were commercial specimens purified by standard methods.

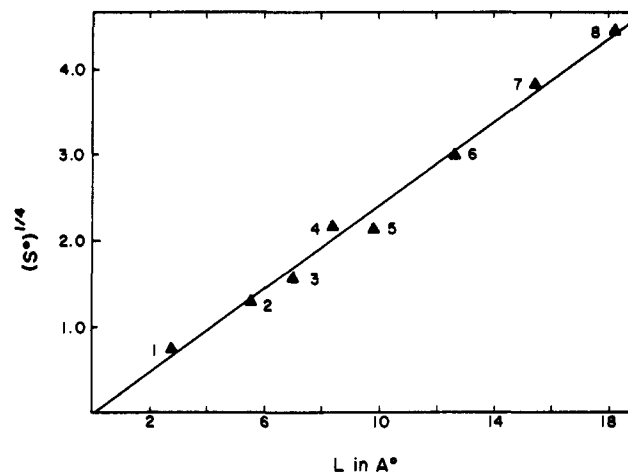
## Results and Discussion

The values of the Raman frequencies, intensities, and depolarization ratios are given in Tables I–IV together with the corresponding transition frequencies ( $\nu_e$ ). Also included are the corrected intensity values ( $S^0$ ) and the length ( $L$  in Å) of the conjugated systems derived as below.

The ( $\nu_8$ ) vibration is comprised of a pair ( $\nu_{8a}, \nu_{8b}$ ) of ring-breathing modes, the coordinates of which are essentially contained in the benzene ring system. The direction of the atomic displacements in the degenerate pair in benzene itself is shown in 1 and 2.



Such diagrams of the forms of the normal modes result from force-field calculations and from a comparison of calculated and observed frequencies for halogenated and deuterated benzenes. The degeneracy is lifted when the symmetry is reduced by attaching even one symmetrical substituent.<sup>17</sup> Calculations show that the forms of the normal coordinates for mono- or disubstituted benzenes are similar to benzene. The infrared intensities of these modes have proved useful<sup>18</sup> in assessing  $\pi$ -electron interactions

(15) Bernstein, H. F.; Allen, G. J. *Opt. Soc. Am.* 1955, 45, 237.(16) Schmid, E. D.; Brosa, B. *Ber. Bunsenges. Phys. Chem.* 1971, 75 (1), 1334.(17) Brownlee, R. T. C.; Katritzky, A. R.; Topsom, R. D. *J. Am. Chem. Soc.*, 1966, 88, 1413.(18) Katritzky, A. R.; Topsom, R. D. *Chem. Rev.* 1977, 77, 639.Figure 1.  $(S^0)^{1/4}$  vs.  $L$  for planar conjugated hydrocarbons.

in substituted benzenes. As there,<sup>17</sup> practical and spectroscopic considerations make it necessary<sup>16</sup> to integrate the intensities of both vibrations together. Raman data for this mode have been reported previously for a considerable number of monosubstituted benzenes<sup>17</sup> and for a series of benzoyl derivatives.<sup>1</sup> It has also been shown that such intensities increase markedly in the series<sup>9</sup>  $\text{C}_6\text{H}_5(\text{CHCH})_n\text{C}_6\text{H}_5$  with an increase in length of the conjugated system but diminish in substituted biphenyls<sup>10</sup> when conjugation is inhibited by sterically induced twisting.

Table I lists Raman data for a series of conjugated hydrocarbons which are expected to be planar. The diphenyl polyenes were the all-trans isomers. These compounds should provide a measure of the dependence of RI on the effective length of the  $\pi$  system in the absence of the polar and charge-transfer effects than can occur in heteroatom systems. The Raman data for the diphenyl polyenes were reported previously,<sup>9</sup> while the value for benzene is a careful redetermination of earlier values.<sup>16</sup> The intensity values are corrected for the number of benzene rings.

As discussed in the introduction, it is important to examine the dependence of these intensities on the exciting frequency, that is on the RRE. It is found that for all compounds measured in this work the intensity variation with change in exciting frequency can be satisfactorily described by use of the  $f_b$  frequency factor alone. Details of the method used have been fully described in an earlier paper.<sup>9</sup> The intensities corrected for the frequency factor ( $S/f_b$ ) are designated  $S^K$ . A related procedure to allow for the RRE is to use an extrapolation procedure to obtain intensities for  $\nu_0 = 0$ . The simplest way to do this is to correct the measured intensities by the factor  $f_b^0/f_b$  where  $f_b^0$  is the value of  $f_b$  when  $\nu_0 = 0$  (that is  $\nu_e^2$ ). One advantage of these values, designated  $S^0$ , is that they are on the same scale as the original intensities. Both the  $S^K$  and  $S^0 (=S^K/\nu_e^2)$  values should be measures of  $K$  (eq 4) that are free from the RRE.

The effective lengths  $L$  of the systems were obtained by adding to the  $\text{C}_1\text{C}_4$  distance in benzene rings (2.80 Å) the standard bond lengths<sup>19</sup> of the  $\text{sp}^2\text{-sp}^2$  carbon-carbon single (1.46 Å) and double (1.34 Å) bonds.

It is found that a plot of either  $(S^0)^{1/4}$  or  $(S^K)^{1/4}$  vs.  $L$  gives a good linear relationship. The plot for the former is shown in Figure 1. The least-squares fitted eq 9 has correlation coefficient

$$(S^0)^{1/4} = 0.244L - 0.032 \quad (9)$$

0.995. The intercept is insignificant, and if the equation is constrained to pass through zero, we obtain eq 10 with the same correlation coefficient. The relation for  $(S^K)^{1/4}$  is given by eq

$$(S^0)^{1/4} = 0.241L \quad (10)$$

11 with correlation coefficient 0.99.

(19) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970; p 111.

$$(S^K)^{1/4} = 36.6L + 64.8 \quad (11)$$

Because of the somewhat better fit and the effectively zero intercept, we have used  $S^0$  values throughout the rest of the work, but our arguments could similarly be based on  $S^K$  values. The inclusion of the  $\nu_e^2$  term in  $S^0$  values also makes allowance for changes in the excitation frequency.

The importance of our results is as follows. Most previous Raman intensity studies have used uncorrected intensity values, and it has been suggested that the increase in  $S$  with larger conjugated molecules has arisen in the frequency factor term as  $\nu_0$  approaches  $\nu_e$ . It was earlier<sup>9</sup> observed that the intensity does seem to increase with the length of conjugation in the absence of the RRE and our results now provide a quantitative relationship. The dependence on  $(S^0)^{1/4}$  means (eq 8) that the derivative of the square of the transition moment with respect to the normal coordinate is proportional to  $(S^0)^{1/2}$ . The length of the conjugated system can by simple theoretical approaches, be linearly related<sup>20</sup> to the transition moment. It follows from eq 8 and 10 that in the present case  $(S^0)^{1/4}$  is proportional to  $M_e$  and  $\partial|M_e|^2/\partial Q$  is linearly related to  $|M_e|^2$ .

It is also worth reiterating that the normal coordinate of the vibration studied is effectively isolated in the benzene ring. The change in polarizability is, however, connected to the charge distribution of the whole molecule, and this changes during the vibration depending on the length of conjugation. A similar situation occurs where the change of dipole moment affects intensities; thus the infrared intensity of the  $\nu_8$  vibration is much greater<sup>21</sup> in  $C_6H_5CHCHCN$  than in  $C_6H_5CN$ .

**Monosubstituted Benzenes.** Several attempts<sup>1-4</sup> have been made to relate the Raman intensities of the  $\nu_8$  variations of monosubstituted benzenes to measures of substituent electronic effects such as Hammett parameters. The only success was the relationship with molar refraction, but some dependence on resonance ( $\pi$ -charge transfer) effects seemed evident. The  $\nu_8$  intensities of benzoyl derivatives  $C_6H_5COX$  were found<sup>1</sup> to be a function of the Hammett substituent constants of the group  $X$ .

We attempted previously to relate the intensities (both  $S^0$  and  $S$ ) to substituent parameters by using the dual substituent parameter (DSP) equation<sup>22</sup> in the form of eq 12, where  $\bar{\sigma}_R$  can have

$$S_X^{1/4} - S_H^{1/4} = \rho_I \sigma_I + \rho_R \bar{\sigma}_R \quad (12)$$

the values<sup>21</sup>  $\sigma_R^+$ ,  $\sigma_R^0$ ,  $\sigma_R$ , or  $\sigma_R^-$ . No satisfactory correlation was found here either when parameters such as  $\sigma^+ - \sigma^0$  were used. However, if  $\pi$ -electron-donating or -withdrawing substituents are considered separately, there is an approximate dependence on their ability to respond to demand as measured by  $\sigma^+ - \sigma^0$  or  $\sigma^- - \sigma^0$  values, respectively.

The work in the previous section suggests that a possible reason for this lack of correlation is a change in the conjugation from one monosubstituted benzene to another. The work of Yoshino and Bernstein<sup>23</sup> has shown that in the vibrating system changes in electron density should lead to intensity changes. The change of polarizability with bond stretching increased in proportion to the bond order in going from CC single to double and to triple bonds. Thus, an effect is expected on Raman intensities where there is a marked change in electron density, but this may be masked by a change in effective length with smaller changes in electron density. Intensity values for heteroconjugated systems such as pyridine are close to those for the hydrocarbon analogue (benzene in the case of pyridine). This suggests that the polar

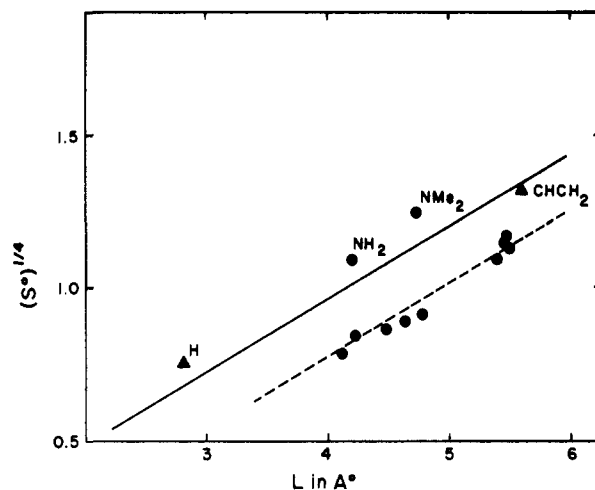


Figure 2.  $(S^0)^{1/4}$  vs.  $L$  for monosubstituted benzenes. The line is from Figure 1.

and charge-transfer effects are relatively small.

We test this assumption by plotting in Figure 2 the  $(S^0)^{1/4}$  values for monosubstituted benzenes (Table II) against  $L$ . The line represents eq 10. The lengths were derived from standard bond lengths as follows: for the halogens, OH, and  $NH_2$  by adding the aryl-X bond length to the 2.80 Å for the benzene ring and for CN, CHO,  $CO_2Me$ , and  $NO_2$  by adding the length of the aryl-carbon or aryl-nitrogen bonds to that of the carbon-nitrogen, carbon-oxygen, or nitrogen-oxygen lengths. The additional value to be used for the addition of a methyl group to benzene, phenol, and aniline (that is, for the compounds toluene, anisole, and dimethylaniline) is not immediately obvious. Clearly, a methyl group attached directly to a conjugated system can increase the effective length through interaction with its CH orbitals of appropriate symmetry (hyperconjugation). We therefore adopted an empirical approach. The  $(S^0)^{1/4}$  value for toluene is 0.134 unit higher than that for benzene corresponding (eq 10) to a increase in length of 0.56 Å. The corresponding value for *trans*- $\beta$ -methylstyrene (1.44 Å) is 0.12 unit higher than that for styrene, corresponding to an increase of 0.50 Å. We therefore have taken an average value of 0.53 Å for the addition of a methyl group. The values of  $L$  are shown in Table II.

Figure 2 shows that while the intensity values for the strongly resonance-donating substituents  $NMe_2$  and  $NH_2$  are somewhat higher than predicted by eq 10, the biggest deviations are for the values below the line. Indeed, the other points, omitting that for toluene which was fitted to the line as described above, lie on an almost parallel (line of best fit to these points has a slope of 0.277, an intercept of -0.38, and a correlation coefficient of 0.991). Table II also lists the deviations ( $C_X$ ) of each  $(S^0)^{1/4}$  value from the value given by eq 10. These differences can arise from several factors such as polar or charge-transfer effects, twisting of the substituent  $\pi$  orbitals relative to those of the benzene ring, or an inaccurate description of the length of errors in the use of a single frequency factor term through eq 4.

The  $C_X$  values are not well fitted by a DSP analysis (eq 12) although an appropriate relationship is observed. We expect to find more accurate relationships for systems either where the length of conjugation is effectively constant or where electronic effects are of greater relative magnitude. We consider two examples below.

**Substituted Biphenyls.** In an earlier paper in this series,<sup>10</sup> it was shown that the  $S$  values for a series of substituted biphenyls could be empirically related to  $\cos^2 \theta$  where  $\theta$  was the angle of twist of one phenyl ring plane relative to the other.<sup>24</sup> The approach above now allows us to make a simple analysis. The values of  $S^0$  are given in Table III. The length of conjugation is the same in each case, 7.06 Å. We use benzene as a model system for the

(20) At "Free Electron" level see: Alonso-Finn "Fundamental University Physics"; Addison-Wesley: Reading, Mass., 1976; Vol. III. At HMO level see: Heilbronner, E.; Bock, H. "Das HMO-Modell und seine Anwendung"; Verlag-Chemie: Berlin, 1970.

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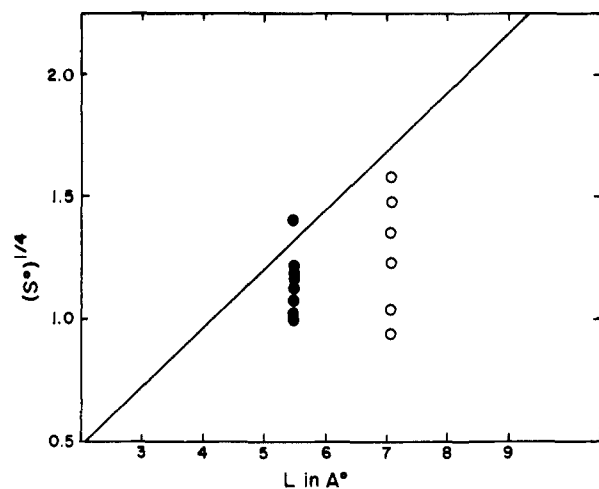


Figure 3.  $(S^0)^{1/4}$  vs.  $L$  for benzoyl derivatives (●) and for substituted biphenyls (○). The line is from Figure 1.

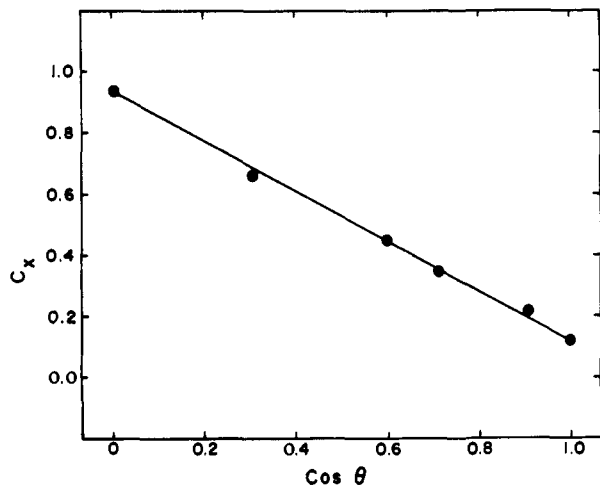


Figure 4.  $C_X$  vs.  $\cos \theta$  for substituted biphenyls.

case of two orthogonal  $\pi$  systems, that is, for an angle  $\theta$  of  $90^\circ$ . It can be seen in Figure 3 that only the value for the planar system, fulvene, lies close to the line of eq 10, the other values being of lower intensity. We can analyze the results in terms of the  $C_X$  values, also listed in Table III. These measure the decrease in conjugation with twisting, and, indeed, a plot of  $C_X$  vs.  $\cos \theta$  is accurately linear as shown in Figure 4. The least-squares analysis gives a slope of  $-0.80$  and a correlation coefficient of  $0.997$ .

**Benzoyl Derivatives.** It was previously observed<sup>1</sup> that with benzoyl derivatives,  $C_6H_5COX$ , there is an approximate relationship between the  $S^{1/2}$  value for the  $\nu_8$  vibration and the Hammett substituent constant,  $\sigma$ , for the group X. In this case,  $C_X$  values measure the change in conjugation between the phenyl

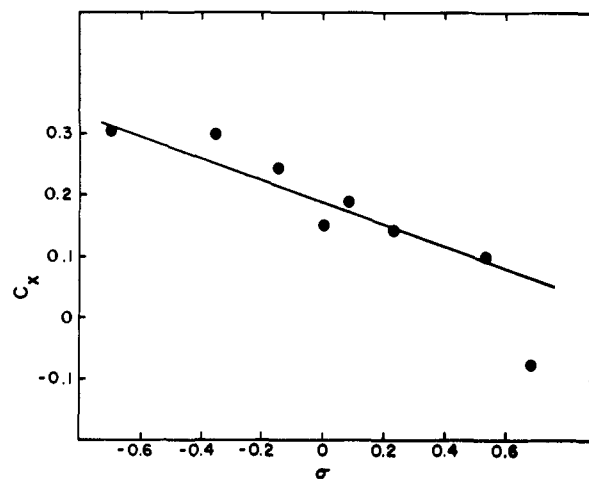


Figure 5.  $C_X$  vs. Hammett  $\sigma$  values for benzoyl derivatives.

ring and the carbonyl group caused by the electronic interaction of the substituent X. We can analyze the corrected intensity values,  $S^0$ , in Table IV, according to our procedure. The length of the system can be taken, to a first approximation, as  $5.48 \text{ \AA}$ , namely, that of the benzoyl group. The  $(S^0)^{1/4}$  values lie below the line of eq 10, as shown in Figure 3. However, the  $C_X$  values (Table IV) give an excellent plot of  $(S^0)^{1/4}$  vs.  $\sigma$ , as seen in Figure 5. The exception is the value for the cyanide substituent, where the length of conjugation may well be extended.

#### Summary

We have established that the fourth root of the Raman intensity is linearly related to the length of conjugation in a series of planar conjugated hydrocarbons, provided that the intensity is corrected for the RRE. This enables us to predict the intensity for other systems, and we describe deviations from such predicted values as  $C_X$  terms for the compounds concerned. Such  $C_X$  values can be related to steric or electronic effects on conjugation for systems where the length of conjugation is approximately constant. The  $C_X$  values for monosubstituted benzenes are not uncorrelated, being negative for strong  $\pi$ -electron donors and positive for strong  $\pi$ -electron acceptors. On the other hand, they cannot be well fitted to electronic substituent parameters. Initial results for disubstituted benzenes<sup>25</sup> with one fixed substituent suggest that such systems will further extend the usefulness of the  $C_X$  values. Here the number of factors affecting the intensity can be reduced by comparison of the results with the corresponding monosubstituted derivatives, as will be discussed in a later paper. The method also promises to provide a measure of the degree of twisting in sterically hindered systems such as biphenyls, styrenes, and stilbenes. We feel that  $C_X$  values are valuable relative quantitative measures of conjugation.

(25) Schmid, E. D.; Topsom, R. D., unpublished results.