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Nonlinear Optical Properties of Organic Molecules. 7. Calculated Hyperpolarizabilities of Azulenes and Sesquifulvalene[1]

John O. Morley

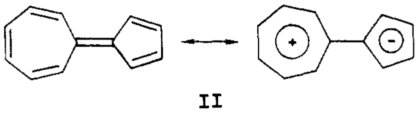
Contribution from the Fine Chemicals Research Centre, ICI Colours and Fine Chemicals, Hexagon House, Blackley, Manchester, M9 3DA, England. *Received February 11, 1988*

Abstract: Calculations are reported on the hyperpolarizabilities of azulene and sesquifulvalene using a CNDO sum-over-states method. The inclusion of at least 30 excited states is required before the values reach stability. The choice of geometry adopted for the calculations on azulene is not critical as similar results are obtained with structures derived from several crystallographic sources. The calculated hyperpolarizabilities are comparable to those obtained for charge-transfer systems such as 4-nitroaniline but show a negative sign which reflects a change of charge transfer from the large ring to the small ring in the ground state to the reverse on excitation. The introduction of substituents which preferentially stabilize the dominant excited state of azulene such as an electron donor in the small ring or an attractor in the large ring results in a substantial increase in the calculated value.

There is growing interest in the design of organic materials with large first hyperpolarizabilities for applications in optical signal processing.[2] The majority of known organic molecules with these attributes contain a strong electron donor and acceptor positioned at opposite ends of a suitable conjugation path;[3] 4-nitroaniline and 4-dimethylamino-4′-nitro-*trans*-stilbene are typical examples. Unfortunately, the presence of polarizing groups of this type usually causes the molecules to crystallize in a centrosymmetric fashion with the result that the prized molecular effect is much reduced or even lost. Furthermore, in one important nonlinear optical application which involves the frequency doubling of the Ga–As semiconductor laser from a fundamental wavelength of 830 nm to a second harmonic of 415 nm, polar molecules of this type show a strong absorption either near to or in the visible region of the spectrum producing destructive absorption of the required wavelength. In contrast, symmetrical nonpolar aromatics, such as naphthalene and anthracene, are transparent in the visible region though few form noncentrosymmetric structures.

The present studies are concerned with a theoretical investigation of aromatic systems with low polarity such as derivatives of azulene (I) or sesquifulvalene (II) which are more likely to crystallize in the desired way and yet polarize on excitation to form charge-separated systems with large hyperpolarizabilities. In addition, the absorption of these molecules is generally weak in the the visible range with typical extinction coefficients of 100–300 in the 580–700 nm range and little absorption in the second harmonic region.[4] Stable derivatives of both systems are known, such as 1,2-bis(methoxycarbonyl)-8,9-diphenylsesquifulvalene,[5] but there are few crystallographic data available for comparative studies.

I



II

The calculations reported here are an extension of previous work and were carried out with the CNDOVSB method[6] which involves an initial configuration interaction treatment of ground (g) and excited state (n and n′) wave functions and then evaluation of the hyperpolarizability tensor from the improved wave functions using the expression:[7]

$$\beta^{2\omega}{}_{ijk} + \beta^{2\omega}{}_{ikj} =$$

$$(-e^3/4\hbar^2)^* \sum_{n'}\sum_{n} \Bigg[(r^j{}_{gn'} r^i{}_{n'n} r^k{}_{ng} + r^k{}_{gn'} r^i{}_{n'n} r^j{}_{ng}) \left\{ \frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - \omega)} \right\} + (r^i{}_{gn'} r^j{}_{n'n} r^k{}_{ng} + r^i{}_{gn'} r^k{}_{n'n} r^j{}_{ng}) \times \left\{ \frac{1}{(\omega_{n'g} + 2\omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)} \right\} + (r^j{}_{gn'} r^k{}_{n'n} r^i{}_{ng} + r^k{}_{gn'} r^j{}_{n'n} r^i{}_{ng}) \left\{ \frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} + 2\omega)} \right\} \Bigg] \quad (1)$$

where $r^i{}_{gn}$ is defined as:

$$r^i{}_{gn} = \langle \Psi_g | \sum_{m=1}^{N} r^i(m) | \Psi_n \rangle \text{ or } \langle g | r^i | n \rangle$$

where $r^i(m)$ is the ith component of the position vector of electron m (of N), $r^i{}_{n'n} = \langle n' | r^i | n \rangle$, ω_{ng} is the eigenvalue of $\Psi_{n'}$ relative to the ground state Ψ_g (the electronic transition energy), e is the magnitude of the electronic charge, and ω is the frequency of the applied radiation field. The indices n and n′ may be restricted to run over excited states in order of increasing energy, provided

$$\langle g | r | g \rangle = 0$$

which holds only in the electronic charge centroid system as previously discussed.[6] The matrix elements, r_{nn}, are then derived in this procedure as the difference between the ground- and excited-state dipole moments, $\Delta\mu$, i.e.,

$$-\Delta\mu/e = r_{nn} = \langle n | r | n \rangle - \langle g | r | g \rangle$$

and rapid convergence of the second-order sum occurs for rep-

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[1] Part 6: Morley, J. O.; Docherty, V. J.; Pugh, D., submitted to *J. Mol. Electron.*

[2] See, for example: *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J. Eds.; Academic Press: New York, 1987.

[3] Morley, J. O.; Pugh, D. ref 2, p 193.

[4] See, for example: Robertson, W. W.; King, A. D., Jr. *J. Chem. Phys.* **1961**, *34*, 2190.

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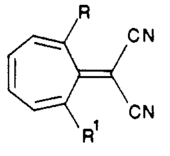
resentative molecules such as aniline and 4-amino-4′-nitrostilbene.[6] All components of the tensor are calculated, though the most relevant quantity, which can be related to experimental data as in previous studies,[1,3,6,8] is the vector component, β_A defined as

$$\beta_A = \beta_{AAA} + \tfrac{1}{3}\sum_i(\beta_{Aii} + 2\beta_{iiA})$$

where β_A is aligned to lie along the direction of the dipole moment. A similar expression can be written for the in-plane vector component β_B which lies in a transverse direction to β_A in the molecular plane. Because the absorption frequencies (ω_{ng}) of azulene and sesquifulvalene sometimes coincide with the second harmonic (2ω) of the applied field of fundamental frequency, ω, there is resonance enhancement of the calculated value of β_A through terms in the denominator of eq 1. Consequently the results reported here are based on the zero frequency, or static field, value β_A as in earlier studies,[1,3,6,8] although eq 1 is an approximate representation when used in this way.[9] However, the results previously calculated at zero frequency using this expression show the same trends as those produced at applied frequencies of either 1.17 or 0.656 eV (for molecules which show no resonance enhancement), thus demonstrating the usefulness of the static field value as an effective measure of the hyperpolarizability.

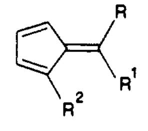
Molecular Templates

An examination of the Cambridge Database[10] shows a number of structures related to the sesquifulvalene. The seven-membered ring of simple heptafulvenes such as the 8,8-dicyano derivative (IIIa)[11] is planar though the introduction of an alkyl group into the 1- or 1,6-positions[12,13] force the bridging carbon containing the exocyclic double bond from the ring plane by torsion angles of ~120°.

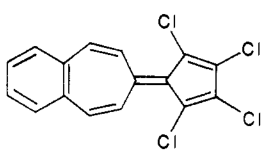


IIIa. R = R^1 = H
b. R = H; R^1 = *i*-Pr
c. R = R^1 = Me

Fulvene systems are invariably planar as illustrated by the 6,6-dimethyl derivative (IVa),[14] but the length of the exocyclic double bond increases sharply if a substituent is present in the 1-position (IVb) from 1.344 in the former to 1.459 A° in the latter.[15] Because the only example of a sesquifulvalene (V) in the database is heavily substituted with an additional aromatic ring and chlorine atoms,[16] the parent molecule (I) was constructed using molecular graphics techniques from the planar 8,8-dicyanoheptafulvene (IIIa) and 6,6-dimethylfulvene (IVa) by removal of the exocyclic substituents and by joining the remaining fragments using a bond length of 1.344 Å.



IVa, R = R^1 = Me; R^2 = H
b, R = Et; R^1 = NEt$_2$; R^2 = -CO$_2$Me



V

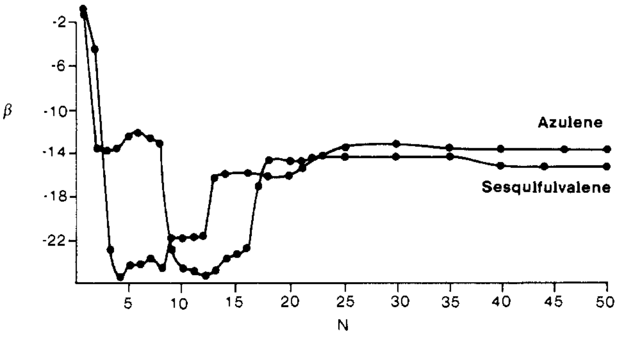
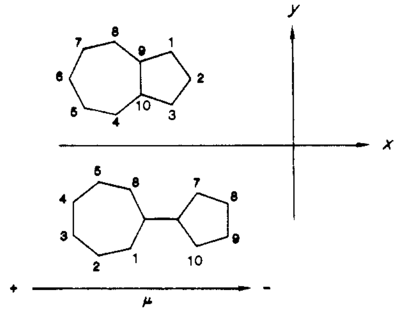


Figure 1. Effect of the number of included states (*N*) on the calculated hyperpolarizability (β_A) of azulene and sesquifulvalene.

Scheme I. Numbering Convention, Selected Coordinate Axes, and the Defined Positive Direction of the Dipole Moment for Azulenes and Sesquifulvalene



In contrast, there are many examples of azulene structures in the database though these are generally substituted with polar groups in either or both rings. In these structures, there are considerable differences in geometry observed for the aromatic ring depending on the nature and positions of the attached substituents (see Table I). For example, the C1–C2 distance varies from 1.372 Å in 2-aminoazulene to 1.434 Å in the 1-tricyanovinyl derivative. Because of the wide variation observed in the bond lengths, a number of derivatives have been selected for study to determine the effect of structure on the calculated results.

For the purposes of calculation all substituents were removed from the azulene ring and replaced by hydrogen atoms using standard bond lengths of 1.08 Å. Trigonal sp^2 nitro- and dimethylamino- groups were inserted using molecular graphics techniques with standard bond lengths of 1.40 Å (Ar–NO$_2$), 1.36 Å (Ar–NMe$_2$), 1.22 Å (N–O), and 1.47 Å (N–CH$_3$). The numbering convention and coordinate axes selected for the calculation of the molecular systems described are shown in Scheme I.

Results and Discussion

The influence of the number of included states (see eq 1) on the calculated hyperpolarizability of sesquifulvalene and azulene is illustrated in Figure 1, and at least 25 excited states are required before the value converges to an optimum. The third excited state is the major contributor to the overall value for azulene though its magnitude is reduced with the inclusion of further states, while the second and ninth excited states are dominant in sesquifulvalene. An analysis of the charge distribution in azulene shows dramatic changes between the ground and third excited state which leads to a reversal in the sign of the *x* component (Scheme I) of the

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Table I. Bond Length Data for Simple Azulenes and Calculated Hyperpolarizabilities for the Parent Hydrocarbon

	Cambridge structure[a] for reference names				
	AMAZUL	AZLNPR	CNVAZL	DAMHEE	STYRAZ
substituents	2-amino	1,3-bis(propionic acid)	1-tricyanovinyl	4,6,8-trimethyl	1,3-bis(styryl)
bond lengths					
C1–C2	1.372	1.415	1.434	1.390	1.400
C2–C3	1.371	1.391	1.349	1.389	1.400
C1–C9	1.390	1.393	1.437	1.383	1.416
C3–C10	1.390	1.415	1.407	1.392	1.416
C4–C10	1.401	1.370	1.392	1.395	1.389
C4–C5	1.386	1.405	1.368	1.372	1.391
C5–C6	1.393	1.384	1.381	1.390	1.380
C6–C7	1.392	1.384	1.384	1.389	1.380
C7–C8	1.410	1.382	1.383	1.374	1.391
C8–C9	1.382	1.389	1.384	1.398	1.389
C9–C10	1.515	1.489	1.464	1.488	1.480
R factor[b]	18.0	8.1	4.1	7.4	4.3
ESD[c]	4	2	2	1	1
β_A (parent)[d]	−12.26	−12.94	−14.65	−12.72	−13.94

[a] The names quoted are unique and taken from the Cambridge Structural Database System (ref 10). [b] *R* factor is a measure of the agreement between the structure as postulated relative to the diffractometer data as collected. [c] Estimated standard deviation in bond length between two heavy atoms. The values are (1) 0.001–0.005 Å, (2) 0.006–0.010 Å, (3) = 0.011–0.030 Å, (4) >0.030 Å. [d] Hyperpolarizability calculated for the parent molecule after replacement of substituents by hydrogen (in units of 10^{-30} cm^5 esu).

Table II. Calculated Dipole Moments[a] and Hyperpolarizabilities[b] of Azulenes and Sesquifulvalene

		x component		*y* component			
structure	substituents	μ_g	μ_e	μ_g	μ_e	β_A	β_B
Ia	none	−3.06	1.93	0	0	−13.94	0
Ib	6-NMe_2	−6.64	−5.74	0	0	−4.43	0
Ic	2-NO_2	−9.10	−5.13	0	0	−9.46	0
Id	1-NMe_2	−0.44	6.34	2.16	2.97	4.54	−24.36
Ie	2-NMe_2	1.20	8.50	0	0	39.77	0
If	4-NO_2	−3.52	0.79	4.78	7.83	−4.54	−12.37
Ig	5-NO_2	1.36	5.79	4.39	6.25	10.62	−16.75
Ih	6-NO_2	3.08	9.13	0	0	16.88	0
Ii	2-NO_2,6-NMe_2	−13.37	−12.19	0	0	2.55	0
Ij	2-NMe_2,6-NO_2	7.92	12.18	0	0	59.89	0
II	none	−6.31	−4.60	0	0	−15.29	0

[a] μ_g and u_e are the ground- and major excited-state dipole moments directed along the *x* or *y* coordinate axis as shown in Scheme I. [b] β_A lies along the direction of the dipole moment and β_B is in the transverse direction in the molecular plane. The values are given in units in 10^{-30} cm^5 esu.

dipole moment from −3.06 to 1.93 D in line with results reported by the Hückel method[17] and more recently by ab initio techniques.[18] The total charges are shown in Figure 2 where the radius of the circle drawn around each atom is proportional to the atomic charge. The large negative charge at the 1- and 3-positions in the ground state are much reduced in the excited state where a large positive charge is now found at the 2-position of the ring. If the charges at the 9– and 10-position of azulene are apportioned equally between the seven- (A) and five-membered (B) rings, the overall ring charges for each respectively changes from +0.2069 (A) and −0.2069 (B) in the ground state to −0.1769 (A) and +0.1769 (B) in the excited state (Figure 2).

A similar transfer of electrons occurs from the small ring to the large ring on excitation from the ground to the second and ninth excited states in the sesquifulvalene, but the magnitude in each case is much less and insufficient to cause a reversal in the sign of the dipole moment (Figure 3). The change in direction of electron transfer on excitation results in a negative sign for the hyperpolarizabilities of each molecule (Table II) at the CNDO/2 level of approximation. A similar result has been reported recently for the sesquifulvalene using the finite field procedure at the MNDO level.[19] The overall magnitude of the calculated hyperpolarizability is comparable to the positive values calculated for highly polar molecules such as 4-nitroaniline although the origin of the effect is different with the latter showing the same direction of electron transfer from the donating amino group

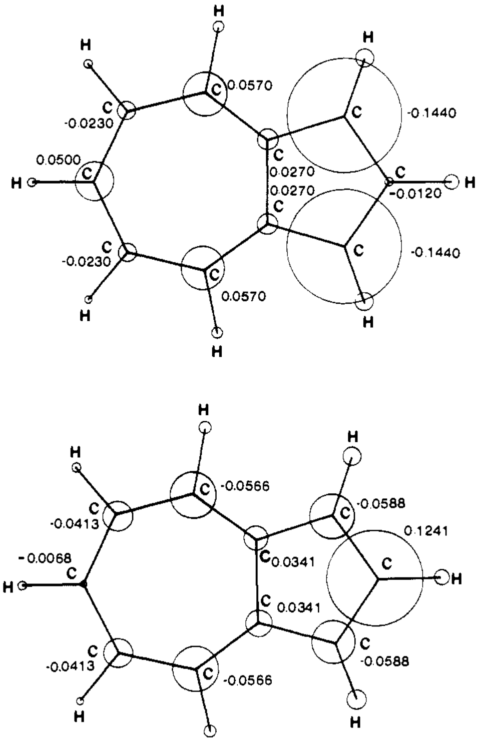

Figure 2. Calculated ground- (above) and excited-state charges (below) in azulene.

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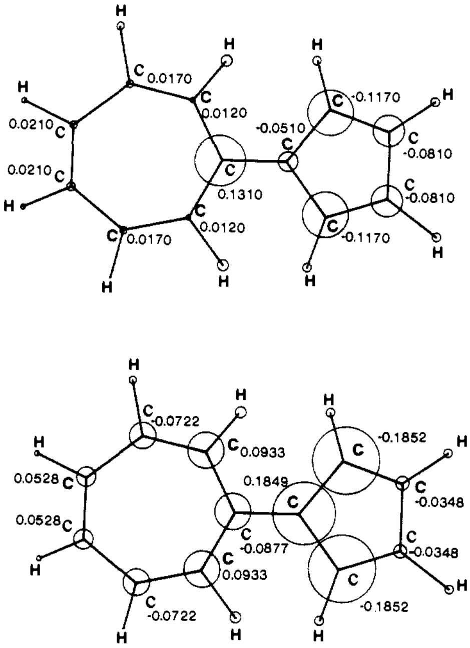

Figure 3. Calculated ground- (above) and excited-state charges (below) in sesquifulvalene.

through the aromatic ring to the nitro group in both ground and excited states.

The geometry of the azulene template adopted for calculation purposes appears to be relatively unimportant as far as the calculated hyperpolarizability is concerned and all five structures selected from the Cambridge Database give approximately the same result (Table I). It seems likely, therefore, that the results for sesquifulvalene, which was constructed from two fragments, are also reliable.

Because the hyperpolarizability is derived in part from the transition moments between ground and excited states (see eq 1), any substituent which is able to stabilize the latter would be expected to enhance its value. It follows that the introduction of an electron donor into the large ring or an electron attractor into the small ring of azulene would be expected to preferentially stabilize the ground state but destabilize the major contributing excited state resulting in a increase and decrease respectively in the magnitude of the dipole moment.

This effect is clearly seen in 6-dimethylaminoazulene (Ib) where the magnitude of the dipole moment increases sharply for the ground state and only decreases slightly for the excited state with a resulting fall in the value of the hyperpolarizability. A similar effect is calculated for 2-nitroazulene (Ic) though less pronounced. In contrast, the introduction of an electron attractor into the large ring or an electron donor into the small ring would be expected to stabilize the excited state and destabilize the ground state, resulting in an increase and decrease, respectively, in the magnitude of the dipole moment. Thus 1- and 2-dimethylaminoazulene (Id, Ie) and the 4-, 5-, and 6-nitroazulenes (If, Ig, Ih) show a sharp increase in the magnitude of the excited-state dipole moment from the ground-state value which arises from a reversal in the direction of charge transfer across the rings. The introduction of both an electron attractor and donor into each end of the molecule produces the expected enhancement of the hyperpolarizability for 2-dimethylamino-6-nitroazulene (Ij) and reduction for 6-dimethylamino-2-nitroazulene (Ii) in line with the arguments developed above.

The calculated results show that the other in-plane vector component of the tensor β_B has a greater value in some cases than that directed along the molecular dipole, β_A (Table II). This arises because the dipole moment is usually aligned along the molecule from left to right in the x direction (Scheme I), but in some cases such as Id, If, and Ig, it is greatest in the direction between the polar substituent and the ring. This is almost the transverse direction in Id and Ig to the direction of electron transfer from the small ring to the large ring on excitation; thus β_A points in these cases roughly along the y-coordinate axis, and the hyperpolarizability is greatest for β_B which now lies along the x-coordinate axis.

It is concluded from the calculations that simple azulene derivatives not only possess substantial hyperpolarizabilities which are comparable to polar organic molecules, but their low dipole moments may favor the formation of noncentrosymmetric crystal forms. These factors combined with their weak absorption in the visible region of the spectrum make them potentially useful as frequency doubling materials.

Registry No. Ia, 275-51-4; Ib, 2048-68-2; Ic, 86760-86-3; Id, 116670-15-6; Ie, 36044-38-9; If, 116670-16-7; Ig, 29906-66-9; Ih, 116670-17-8; Ii, 116670-18-9; Ij, 116670-19-0; II, 1961-84-8.