Non-linear Optical Properties of Organic Molecules. Part 8.[1] Dipole Moments and Hyperpolarisabilities of Some Substituted Azulenes and Aza-azulenes

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Semi-empirical and *ab initio* calculations are reported on the dipole moments and hyperpolarisabilities of azulenes and aza-azulenes based on structures derived either from crystallographic data or from STO-3G optimisations. A comparison between calculated and experimental dipole moments suggest that the amino group in 2-aminoazulene is tetrahedral while that in the corresponding 2-acetamido derivative is trigonal. The results show that the dipole moment of the azulene ring can be adjusted to favour possible non-centrosymmetric crystal forms by inserting nitrogen into the ring in place of carbon without markedly changing the magnitude of the large calculated hyperpolarisability.

A considerable number of calculations have been reported on the hyperpolarisability of conjugated organic molecules and a number of potentially interesting systems have been discovered which have important applications in non-linear optics as frequency doublers or phase modulators.[2,3] Most polar molecules with large hyperpolarisabilities which are useful for these applications, however, crystallise in a centrosymmetric fashion and the high molecular values are much reduced or even lost in the solid state.[3] Recent calculations have suggested that simple azulenes or sesquifulvalenes should possess values which are comparable, though of negative sign, to highly polar systems such as 4-nitroaniline yet are more likely to crystallise in a non-centrosymmetric fashion because of their relatively low dipole moments.[1] While the structure of azulene itself is disordered,[4] its relatively large calculated hyperpolarisability has been rationalised in terms of a change in the direction of electron transfer from the large ring to the small one in the ground state to the reverse in the excited state.[1] Substituents such as 2-dimethylamino- and 6-nitro-groups, which preferentially stabilise the excited state, greatly enhance the hyperpolarisability but also result in an increase in the ground-state dipole moment.[1] Although this effect may favour the formation of centrosymmetric crystals in certain cases, simple derivatives such as 2-aminoazulene are non-centrosymmetric.[5]

The work described here is concerned with the effect of introducing selective substituents or heteroatoms such as nitrogen into the azulene ring with the objective of adjusting the ground-state dipole moment to favour non-centrosymmetric packing while maintaining the relatively large hyperpolarisability calculated for azulene itself.[1] However, because the calculated dipole moments at the semi-empirical CNDOVSB level are generally overestimated,[2] additional calculations have been carried out on azulenes with known experimental values, at both the semi-empirical and the *ab initio* STO-3G and 4-31G levels so as to provide a reliable method for predicting values in speculative derivatives or heterocyclic analogues. The molecules calculated include 1-, 2-, 5-, and 6-aza, and 5,7-diaza-azulenes as well as 1-nitro-, 2-amino-, 2-acetamido-, 2-chloro-, 2-cyano-, and 1,3-dichloro-azulenes.

As in previous cases, all components of the hyperpolarisability tensor are calculated by the sum-over-states procedure,[1,2] but the most relevant quantity which can be related to experimental studies using the technique of electric-field induced second harmonic generation in solution, is the vector component,[2] β_A, defined as

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

where β_A is aligned to lie along the direction of the molecular dipole moment. A similar expression can be written for the transverse in-plane vector component β_B. Because the absorption frequency of the substituted azulenes sometimes coincides with the second harmonic frequency of the incident field, resulting in resonance enhancement of the hyperpolarisability, the results given here relate to the static field values only as in previous cases[1,2] using 50 states for the calculation.

Molecular Templates.—Although there are a number of simple azulene structures present in the Cambridge crystallographic database,[6] no co-ordinates are available for the parent itself. A template for azulene (**1**) was generated, therefore, from the symmetrical 1,3-distyryl derivative[7] which is better resolved than alternatives such as the 1-tricyanovinyl[8] or 4,6,8-trimethyl[9] derivatives, by replacing the styryl groups with hydrogen using molecular-graphics techniques which have been described previously.[2] 1-Nitro- (**2**), 2-chloro- (**3**), 2-cyano- (**4**), and 1,3-dichloro- (**5**) azulenes were constructed by adding nitro, chloro, and cyano substituents to the parent template using standard bond lengths of 1.47 ($Ar-NO_2$), 1.23 (N=O), 1.71 (Ar–Cl), 1.45 (Ar–CN), and 1.16 Å (–C≡N).* Co-ordinates for 2-aminoazulene (**6a**) and (**6b**) were taken directly from the database[5,6] though only heavy atoms are present. Missing hydrogens were added using standard bond lengths of 1.08 Å to the aromatic ring (with appropriate angles) and 0.95 Å to an assumed trigonal sp^2 nitrogen. 2-Acetamidoazulene (**7a,b**) was constructed from the amino derivative (**6**) by adding the acetamido group using bond lengths of 1.32 ($ArNHCOCH_3$), 1.40 (NH–CO), 1.22 (C=O), and 1.52 Å ($OC-CH_3$). 1-Aza- (**8**), 5-aza- (**10**), and 5,7-diaza- (**12**)-azulenes were generated from the crystal structures of the 2-chloro-1-aza-,[10] 5-aza-6-*N*,*N*-dimethylamino,[11] and 5,7-diaza-6-*N*,*N*-dimethylamino-[12] derivatives, respectively, by replacing the substituents by hydrogen as before. Structures for 2-aza- (**9**) and 6-aza- (**11**)-azulenes which are unknown were generated from empirical structures by STO-3G optimisations which allowed all variables to change except the C–H bond lengths which were fixed at 1.08 Å and the torsional angles of the ring which were assumed to be planar. The results obtained are illustrated in the Figure.

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* Based on average values from the Cambridge Structural Database.

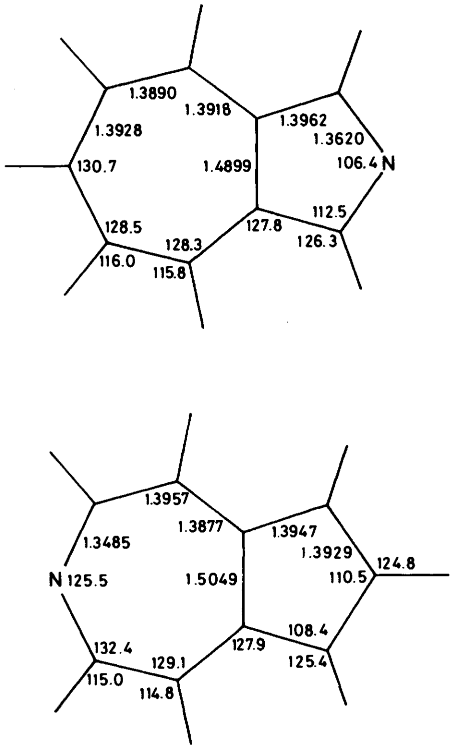
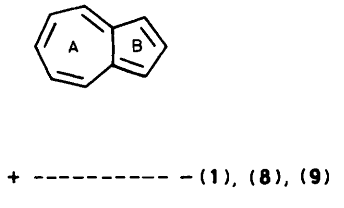


Figure. Calculated geometries of 2-aza- and 6-aza-azulene using the STO-3G method

Results and Discussion

The calculated dipole moments (μ) for azulene itself are overestimated at all levels of approximation particularly for the semi-empirical method (Table 1). While similar results have been reported at the STO-3G and 6-31G levels on calculated structures (μ = 1.81 and 1.73 D* respectively),[13] the inclusion of electron correlation at the MP2/6-31G level is required (μ = 1.23 D)[13] before the experimental value (μ = 1.08 D)[14] is approached. Similar trends are observed with the chloro-azulenes (**3**) and (**5**) which show larger calculated values than expected at all levels of approximation explored in the present work. However, the introduction of the nitro- and cyano-group into the 1- and 2-position, respectively, of azulene stabilises the electron transfer from the large ring to the small one in the ground state resulting in a sharp increase in the dipole moment which is well reproduced by the STO-3G method but is overestimated by the usual amount at the semiempirical level. In contrast, calculations on 2-aminoazulene show a considerable underestimation of the dipole moment at all levels including the 4-31G level relative to the experimental data (Table 1). Although a planar structure (**6a**) had been expected for the molecule in solution, repeat calculations carried out on an alternative structure (**6b**), obtained by adding hydrogen atoms to an sp^3 tetrahedral nitrogen, gave vastly improved values for all three methods (Table 1). It is clear, therefore, that the amino-group of 2-aminoazulene adopts a tetrahedral conformation in a similar way to that of aniline.[15] The corresponding results for 2-acetamidoazulene, however, show the opposite effect in that the dipole moments strongly support an sp^2 structure (**7a**) with a trigonal nitrogen attached to the azulene ring instead of the alternative sp^3 type. This interpretation is supported by the crystallographic data for acetanilide[16] which shows a planar acetamido group with an sp^2 nitrogen though the group is twisted approximately 18° from the ring plane. It follows that an electron-attracting carbonyl group situated adjacent to an amino group is sufficient to lock the nitrogen into an sp^2 conformation even though the same atom is also conjugated with an electron-rich aromatic ring. Previous calculated results on 2-dimethylaminoazulene, which show the dimethylamino-group stabilising the excited state and enhancing the hyperpolarisability by sp^2 conjugation, now seem unlikely.[1] Indeed, an analysis of the charge distribution in the sp^3 model of 2-aminoazulene shows little transfer of charge from the amino group to the ring with the result that there is little stabilisation of the excited state and little enhancement of the hyperpolarisability which retains the same negative sign in this case as that calculated for azulene itself. For example, if the charge at the 9- and 10-positions of 2-aminoazulene ring is apportioned equally between the large (A) and small (B) rings the overall ring charges for each, change from +0.1347 (A) and −0.1347 (B) in the ground state to −0.2043 (A) and +0.2043 (B) in the dominant excited state (which is the major contributor to the hyperpolarisability[1]) in a similar way to azulene itself. The major component of the dipole moment of 2-aminoazulene arises from the out-of-plane μ_z contribution of the nitrogen atom (Table 2). The results from these studies show that the *ab initio* methods generally give a reasonable description of the dipole moment of substituted azulenes containing polar groups which should extend, in principle, to the aza-azulenes which have no experimental values.

It was expected that the nitrogen atom present in the aza-azulenes would produce an effect similar to that of the electron attracting cyano group in azulene itself with substitution in the small ring increasing the dipole moment by stabilising the electron donation from the large ring to the small one in the ground state, with the converse effect produced for substitution in the large ring. The results of the calculations show that the influence of the nitrogen atom is less marked than expected; 1- and 2-aza-azulenes [(**8**) and (**9**)] show dipole moments which are approximately midway between azulene and 2-cyanoazulene (Table 1) with the nitrogen atom producing the expected increased polarisation of the ground state accompanied with a reversal of charge transfer upon excitation (Table 2). The calculated hyperpolarisability for 2-aza-azulene (**9**) is comparable to that of azulene, though the 1-aza-analogue (**8**) has two components of approximately equal magnitude though reversed in sign (Table 2). This arises because the hyperpolarisability tensor is rotated to point along the direction of the molecular dipole moment,[2] which lies, in symmetrical cases, in one direction along a horizontal line from left to right between the large ring and the small one (Scheme).



Scheme. Direction of the dipole moment in symmetrical aza-azulenes

In unsymmetrical cases, however, the hyperpolarisability tensor β_A, is rotated to point along the vector of the two components, μ_x, and μ_y, which lie in the molecular plane. There are, therefore, two components to the hyperpolarisability, one of which corresponds to the direction of the dipole moment while the other lies in the transverse direction.

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* 1 Debye ≈ 3.335 64 × 10^{-30} C m.

Table 1. A comparison between calculated and experimental dipole moments for azulenes

		Dipole moment/D				
Substituent	Structure	CNDOVSB	STO-3G	4-31G	Exptl	Reference
None	**(1)**	3.06	1.88	1.81	1.08	14
1-Nitro	**(2)**	8.06	6.06	8.13	6.06	14
2-Chloro	**(3)**	6.66	4.69	4.28	2.69	17
2-Cyano	**(4)**	7.99	6.25	7.59	5.68	17
1,3-Dichloro	**(5)**	6.26	4.52	3.98	2.45	14
2-Amino-(sp^2)	**(6a)**	0.25	0.38	0.60	2.09	17
2-Amino-(sp^3)	**(6b)**	2.15	1.65	1.85	2.09	17
2-Acetamido-(sp^2)	**(7a)**	4.14	2.07		3.26	17
2-Acetamido-(sp^3)	**(7b)**	2.86	1.17		3.26	17
1-Aza	**(8)**	4.32	2.76	3.52		
2-Aza	**(9)**	6.10	4.48	5.23		
5-Aza	**(10)**	2.58	1.62	2.08		
6-Aza	**(11)**	0.36	0.77	1.62		
5,7-Diaza	**(12)**	0.91	0.99	2.46		

Table 2. Calculated components of the dipole moment (μ) and hyperpolarisabilities (β) of azulenes[a]

	x-Component			y-Component				
Structure	μ_g	μ_e	$\Delta\mu$	μ_g	μ_e	β_A	β_B	β_{vec}
(1)	−3.06	1.93	4.99	0	0	−13.94	0	13.94
(2)	−5.72	−2.13	3.59	−5.67	−6.32	−6.21	10.68	12.36
(3)	−6.65	0.28	6.93	−0.17	0.01	−14.52	0	14.52
(4)	−7.98	−2.08	5.90	−0.21	−0.05	−14.72	0	14.72
(5)	−6.26	−0.22	6.04	−0.17	−0.01	−14.45	0	14.45
(6b)	−0.56	5.05	5.61	−2.06[b]	−0.22[b]	−12.00	−16.35	21.60
(7a)	1.32	8.03	6.71	−3.90	−3.56	8.03	21.63	23.08
(8)	−3.11	1.77	4.88	−2.99	−2.82	−6.09	7.58	9.72
(9)	−6.10	−1.65	4.45	0	0	−11.22	0	11.22
(10)	−1.66	3.44	5.10	1.97	0.99	−8.93	−12.50	15.37
(11)	0.36	5.05	4.70	0	0	11.82	0	11.82
(12)	0.87	5.24	4.37	−0.05	−0.05	12.77	0.50	12.78

[a] $\Delta\mu$ is the difference between the ground (μ_g) and excited state (μ_e) dipole moments. In most cases the major components lie along the in-plane x- and y-axes except for the 2-amino derivative where the perpendicular component μ_z is dominant (see text); small z-components found in a number of derivatives derived from crystallographic data have been omitted. β_A, β_B, and β_{vec} are defined in the text and are expressed throughout in units of 10^{-30} cm^5 e.s.u. [b] The perpendicular μ_z component is shown in place of the small μ_y value.

In contrast, 5-aza-, 6-aza- and 5,7-diaza-azulene [**(10)**, **(11)** and **(12)**] have lower ground-state dipole moments than either azulene or the 1- or 2-aza-analogues because the electron transfer from the large ring to the small one is counteracted by the electron-attracting nitrogen(s) in the large ring, resulting in a reversal of charge transfer in the ground state. This is illustrated by the change of sign in the x-component of the dipole moment in moving from 2- to 6-aza- and 5,7-diaza-azulene. The calculated hyperpolarisabilities reflect this change with the latter now showing positive values since there is no reversal or reduction in magnitude in the change from ground to excited state. An analysis of the change in dipole moment ($\Delta\mu$) on moving from the ground state to the dominant excited state shows little variation from azulene to the aza-azulenes (Table 2). Similar trends are observed for the vector of the hyperpolarisability tensor β_{vec} where and β_C is the perpendicular

$$\beta_{vec} = (\beta_A^2 + \beta_B^2 + \beta_C^2)1/2$$

component of the rotated tensor. In this case the values obtained for the unsubstituted azulenes [**(1)**, **(8)**—**(12)**] are roughly comparable to each other with the exception of the 5-aza-analogue.

Although the low semi-empirical dipole moment ($\mu = 0.35$ D) of 6-aza-azulene suggests that the molecule is more likely than azulene to crystallise in a non-centrosymmetric fashion, the 4-31G results ($\mu = 1.62$ D) indicate that the values are comparable though in opposite directions. However, there is strong evidence to suggest that the STO-3G results which fall between these values ($\mu = 0.77$) may give a better representation of the atomic charges for π-electron systems.[18] Overall, the results show that the dipole moment of azulenes can be tuned, by a careful selection of substituents and/or by the insertion of nitrogen into either ring, to favour non-centrosymmetric crystal forms, without markedly reducing the magnitude of the hyperpolarisability.

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Received 26*th April* 1988; *Paper* 8/01645