

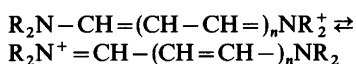
## Rotational Barriers in Cyanine Dyes: *Ab initio* Studies of Some Simple Diamino-polymethinium Cations

S. SÆBØ and J. ALMLØF

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

Some simple model compounds for cyanine dyes have been investigated using *ab initio* methods, with particular emphasis on rotational barriers about the CN bonds. Complete geometry optimizations have been performed using an efficient gradient technique. It is shown that a full geometry relaxation of the rotated forms must be allowed in order to reproduce the experimentally observed trend of decreasing barrier with increasing chain length.

For some time, cyanine dyes have attracted theoretical interest insomuch as their electronic structure cannot be represented by one single classical valence-bond form. Two equivalent mesomeric structures,



are in fact needed for the valence-bond description, and accordingly the CN bonds are expected to show a partial double-bond character. The rotational barriers about these CN bonds have been experimentally determined,<sup>1</sup> and showed a rather rapid decrease of barrier height with increasing chain length.

Several different explanations are possible for this effect. The experimental data were all obtained in the liquid phase, and obviously ion pairs are likely to occur in the solution. With the anion close to one end of the chain the mesomeric form with a positive charge at that end will be favoured, and the CN double-bond character at the opposite end will then decrease. Such an asymmetric arrangement can occur more easily if the chain length increases, and this could thus explain the observed trend.

The present calculations have all been performed

for the free cation only, and are obviously incapable of describing the above ion pairing. On the other hand, if such calculations are indeed able to reproduce the trend in barrier heights, one may assume the effects of ion pairing on these barriers to be of little importance.

When seeking explanations of the above phenomenon in terms of properties of the free ion only, one may first investigate whether a change of the chain length affects the CN bond orders. However, these were found to be rather constant (60–70% double-bond character) in previous semi-empirical calculations.<sup>2</sup> This is not very surprising, and evidently great care must be exercised when conclusions about rotational barriers are made on the basis of properties for the planar system only.

### CALCULATIONS

In order to resolve the above seeming contradiction the present investigations were made. A series of model compounds,  $NH_2(CH)_{2n+1}NH_2^+$  with  $n=0, 1, 2, 3$ , were studied with *ab initio* methods. For some of the molecules, the number of independent geometry parameters is too large to make a conventional geometry optimization (by means of pointwise calculated energies) feasible. The recently developed gradient method,<sup>8</sup> allowing a simultaneous relaxation of the forces on all atoms in the molecule, was therefore used instead. The calculations employed a double-zeta basis of contracted Gaussians<sup>3,4</sup> and programs developed in our group were used.<sup>5–7</sup>

For the mono-, tri- and pentamethinium compounds ( $n=0, 1, 2$ ) full geometry optimizations were performed, starting with the planar compounds. The geometry for the heptamethine species could

Table 1. Total energies (in Hartrees) for the planar form and rotational barriers (in  $\text{kJ mol}^{-1}$ ) for the polymethinium cations  $\text{NH}_2(\text{CH})_{2n+1}\text{NH}_2^+$ .

<i>n</i>	$E_{\text{tot}}$	Calc. <sup>a</sup>	Calc. <sup>b</sup>	Exp. <sup>c</sup>
0	-149.2743	142	120	70
1	-226.0887	171	124	74
2	-302.0971	166	109	59
3	-379.7022	164	99	49

<sup>a</sup> Calculated with frozen geometry. <sup>b</sup> Calculated with full geometry relaxation. <sup>c</sup> From Ref. 1.

then be rather accurately deduced by extrapolating values for the optimized distances and angles. As for the previous semi-empirical calculation,<sup>2</sup> the character of the CN bonds changed very little through the series. One of the terminal  $\text{NH}_2$  groups was then twisted by  $90^\circ$ , and the energy was re-

computed without relaxing the geometry for the rest of the molecule (test calculations revealed that a twist of  $90^\circ$  really corresponded to the maximum of the barrier). However, the estimates for rotational barriers obtained in this way showed very small variation with chain length (except for the monomethine compound, which behaves abnormally in the series in many respects due to the strong steric repulsion between the  $\text{NH}_2$  groups in the planar form). From these results it is thus evident that the relaxation of the electronic system upon rotation, leading to only one of the mesomeric forms for the  $90^\circ$  geometry, does not become more important when the chain is longer.

Keeping the twist angle fixed to  $90^\circ$  the geometries were therefore reoptimized. Again the geometry for the heptamethine compound was deduced by extrapolation on the values obtained by optimizing the smaller compounds. The corresponding energies

Table 2. Bond distances (in Å) and angles (in degrees) for the planar and rotated forms of the diaminopolymethinium cations. In cases where several values are given the ordering is from the  $\text{NH}_2$  end towards the middle for the planar ( $C_{2v}$ -symmetric) form, and from the planar  $\text{NH}_2$  group towards the rotated one for the non-planar case. The values for  $n=3$  were not optimized. Although structurally non-equivalent, the optimized NH and CH distances and the HCC angles showed only small variations within the same molecule. The table entries for  $n=0, 1$  and  $2$  in these cases show only the mean value and the maximum deviation. For  $n=3$  one fixed value was used.

<i>n</i>	$R_{\text{NH}}$	$\theta_{\text{HNH}}$	$\theta_{\text{NCH}}$	$R_{\text{CN}}$	$R_{\text{CC}}$	$R_{\text{CH}}$	$\theta_{\text{HCC}}$
Planar case							
0	$1.000 \pm .001$	115.9	117.6	1.303	—	1.064	—
1	$0.998 \pm .001$	116.3	115.0	1.311	1.379	$1.071 \pm .002$	$119.8 \pm .2$
2	$0.996 \pm .001$	116.5	114.7	1.318	1.375	$1.073 \pm .003$	$119.8 \pm .2$
					1.383		
3	0.995	116.5	114.6	1.32	1.373	1.074	119.8
					1.380		
					1.385		
Twisted case							
0	$1.004 \pm .002$	115.9	120.0	1.273	—	1.075	—
		124.5	120.8				
1	$1.001 \pm .002$	116.4	116.4	1.290	1.422	$1.075 \pm .006$	$119.5 \pm .4$
		120.1	120.1	1.399	1.335		
2	$0.998 \pm .001$	115.9	116.5	1.295	1.413	$1.074 \pm .006$	$118.5 \pm 1.0$
		123.8	119.4	1.403	1.352		
					1.435		
					1.331		
3	0.997	116.0	116.5	1.300	1.410	1.074	118.5
		124.0	119.0	1.410	1.350		
					1.410		
					1.350		
					1.440		
					1.330		

and rotational barriers are presented in Table 1. Evidently, the relaxation of the geometry rather than of the electronic system seems to be the phenomenon responsible for the change in rotation barriers. The final geometry parameters are presented in Table 2. In order to find a simple, qualitative explanation of the trend, we note that the CC bond distances change by an amount of  $\sim 0.04$  Å upon geometry relaxation. This value appears to be reasonably constant through the series, within the limits studied here. Assuming the CC stretching force constants to be constant as well, it is then easily explained why the geometry relaxation effect becomes more important when the chain length increases.

## CONCLUSION

*Ab initio* SCF calculations with a basis set of double-zeta quality have proven capable of describing the decrease in rotational barriers with increasing chain length for the series of polymethinium dyes studied here.

It has been shown that the trend is due to the geometrical relaxation of the chain upon rotation. This effect becomes more important when the chain length increases. In contrast, the effects of electronic rearrangements when a terminal group is rotated is almost independent of the chain length, assuming a frozen geometry. The necessity for complete geometry optimization in problems of this type has been demonstrated.

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