Tetrahedron Vol. 34, pp. 3225–3232
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0040-4020/78/1101-3225/$02.00/0

POLARIZED ABSORPTION SPECTRA OF SOME ELECTRON-DONOR-ACCEPTOR CYCLOPHANES[1-3]

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(*Received in UK* 17 *March* 1978; *Accepted for publication* 12 *June* 1978)

Abstract—The polarized absorption spectra for single crystals of two isomeric electron-donor-acceptor (EDA) cyclophanes were measured in the visible region. The charge-transfer character of the visible absorption was confirmed from the polarization data as well as from correlation with the results of P.P.P. type calculation based on crystal structural data. The calculations furthermore allowed separation of the contributions from inter- and intramolecular donor-acceptor interactions to the overall charge-transfer absorption.

Charge transfer (CT) or electron donor-acceptor (EDA) interaction plays an important role in many fields of chemistry and biology as discussed in various reviews.[4-6]

As part of our investigations on the conformational requirements for EDA interaction, we synthesized[2,7] a number of cyclophanes containing within one molecule a π-electron donor- and a π-electron acceptor system interconnected by two polymethylene chains. In earlier publications[1,3] we presented preliminary reports about the dramatic influence of the length of the methylene chains on the intramolecular CT absorption[1] and emission[3] of some of these EDA cyclophanes in solution.

Since then several other groups have reported[8-10] the syntheses and spectroscopic behaviour of EDA cyclophanes. The latter studies have been focussed mainly on [2.2]-(EDA)-cyclophanes (see Ref. 11) for which the large distortion[12] of the aromatic systems and the occurrence of extensive through-bond interaction[13] complicate the interpretation of the spectroscopic data.

Recent investigations[14] have stressed the importance of through-bond interaction between an electron donor and an electron acceptor separated by two saturated C-atoms in the description of the electronic spectra of such compounds. The occurrence of through-bond interaction in [2.2]-(EDA)-cyclophanes means, that the overall degree of donor-acceptor interaction will not only depend upon the relative spatial positions of D and A but also on the topology of their interconnection.

The present paper deals with the spectroscopic properties of the two cyclophanes depicted in Fig. 1 for which the synthesis, systematic nomenclature as well as a shorthand notation ([6.6]D_pA_N and [8.4]D_pA_N) have been discussed earlier,[2,7] whereas their crystal structural data have become available recently.[15]

RESULTS AND DISCUSSION

Crystal structures. Since a detailed account of the crystal structure determinations will be given elsewhere[15] only some pertinent data are compiled in Table 1.

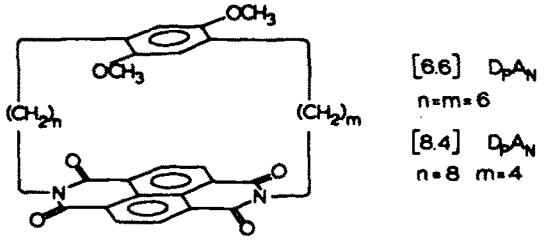


Fig. 1. Structure and shorthand notation of the EDA-cyclophanes studied.

Within the limits of error the D and A systems are planar both in [8.4]D_pA_N and in [6.6]D_pA_N. Furthermore the molecules are stacked according to $\underline{D\ \overline{A}}\overline{\ \ }\underline{\overline{D}\ \overline{A}}\overline{\ \ }\underline{\overline{D}\ A}$ with the molecular planes of D and A nearly parallel for both the intramolecular and the intermolecular contacts. The stacking direction coincides very nearly with the crystallographic c-axis for [6.6]D_pA_N and with the a-axis for [8.4]D_pA_N.

The crystals of [8.4]D_pA_N show disorder due to the presence of two slightly different molecular conformations (designated I and II) in a ratio of about I/II = 4. As a result the crystal structural data for [8.4]D_pA_N are rather imprecise.

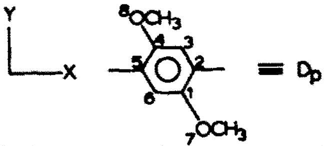
In the quantum mechanical calculations (*vide infra*) the internal coordinates of the D and A moieties for [8.4]D_pA_N were therefore assumed to be identical to those determined for [6.6]D_pA_N, which are given in Table 2.

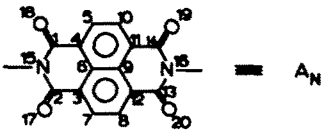
Optimal fit of these internal coordinates to the crystal structural data leads to the six donor-acceptor orientations which are defined in Fig. 2 relative to the internal coordinates of the acceptor system (i.e. one intramolecular and one intermolecular orientation for [6.6]D_pA_N and two such sets with a population ratio 4:1

Table 1. Crystal structural data for EDA cyclophanes[15]

cyclophane	morphology	cell constants
$[6.6]D_pA_N$	monoclinic; $P2_1/c$ four molecules per unit cell	a = 9.288 Å b = 20.976 Å c = 14.866 Å β = 100.30°
$[8.4]D_pA_N$	orthorhombic; Pbca eight molecules per unit cell	a = 14.91 Å b = 17.56 Å c = 24.15 Å

Table 2. Internal coordinates determined by X-ray analysis for the D and A systems in $[6.6]D_pA_N$





	Coordinates (Å)			Coordinates (Å)			Coordinates (Å)	
Atom	**X**	**Y**	**Atom**	**X**	**Y**	**Atom**	**X**	**Y**
1	0.6725	-1.1784	1	-2.8773	1.2217	11	1.3901	1.2412
2	1.4088	0.0000	2	-2.8642	-1.2405	12	1.4023	-1.2189
3	0.6902	1.1844	3	-1.3896	-1.2316	13	2.8820	-1.2232
4	-0.6907	1.1891	4	-1.3962	1.2152	14	2.8795	1.2242
5	-1.4087	0.0000	5	-0.7050	2.4037	15	-3.5267	-0.0211
6	-0.7026	-1.1837	6	-0.7068	0.0000	16	3.5309	0.0148
7	1.4326	-2.3436	7	-0.6954	-2.4135	17	-3.5110	-2.2812
8	-1.4488	2.3412	8	0.7138	-2.4045	18	-3.5171	2.2490
			9	0.7068	0.0000	19	3.5017	2.2813
			10	0.6875	2.4138	20	3.5271	-2.2413

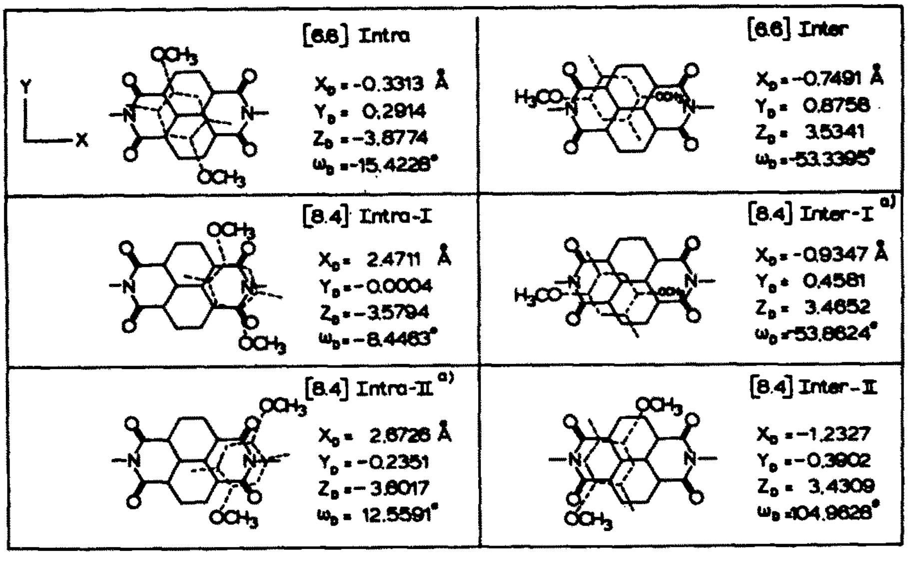


Fig. 2. Relative orientations of the donor moiety towards the acceptor in crystals of $[6.6]D_pA_N$ and $[8.4]D_pA_N$ as defined by the displacement (x_D, y_D, z_D) and rotation in the xy plane (ω_D) of the local donor coordinates (see Table 2) relative to the acceptor coordinates [a](the x-coordinates of the donor are the negative of those given in Table 2).

for [8.4]D$_p$A$_N$). The relations between the internal coordinate axes of the acceptor and the crystallographic axes are given by the following transformations:

$$[6.6]\mathrm{D_pA_N}\begin{pmatrix}X\\Y\\Z\end{pmatrix}=\begin{pmatrix}-0.5548 & -0.8250 & -0.0078\\-0.8193 & +0.5642 & +0.0455\\-0.1459 & -0.0321 & +0.9989\end{pmatrix}\begin{pmatrix}a\\b\\c\end{pmatrix}$$

$$[8.4]\mathrm{D_pA_N}\begin{pmatrix}X\\Y\\Z\end{pmatrix}=\begin{pmatrix}+0.1794 & +0.4870 & +0.8548\\+0.2294 & +0.8242 & -0.5178\\-0.9567 & +0.2890 & +0.0362\end{pmatrix}\begin{pmatrix}a\\b\\c\end{pmatrix}$$

Polarized absorption spectra. Rectangular thin plate like crystals of both cyclophanes were investigated by microspectrophotometry (see Experimental) in the visible region.

Because of the low crystal density and the relatively weak visible absorption these crystals proved particularly suitable for the measurement of polarized spectra. As evident from the spectra (see Figs. 3 and 4) the crystals show strong dichroism due to the presence of a broad absorption band polarized along the elongated direction of the crystals, which coincides with the c-axis for [6.6]D$_p$A$_N$ and with the a-axis for [8.4]D$_p$A$_N$.

The visible absorption passes through a minimum when the light is polarized perpendicular to the elongated direction (i.e. along the b-axis in both cases), the polarization ratios being 4.3 and 8 for [6.6]D$_p$A$_N$ and [8.4]D$_p$A$_N$ respectively. Thus, the polarization of the visible absorption coincides with the stacking direction of the D and A systems which strongly supports the CT-character of this absorption. At shorter wavelength the absorption is apparently more polarized in the plane of the D and A moieties and thus has the character expected for local transitions within these chromophores.

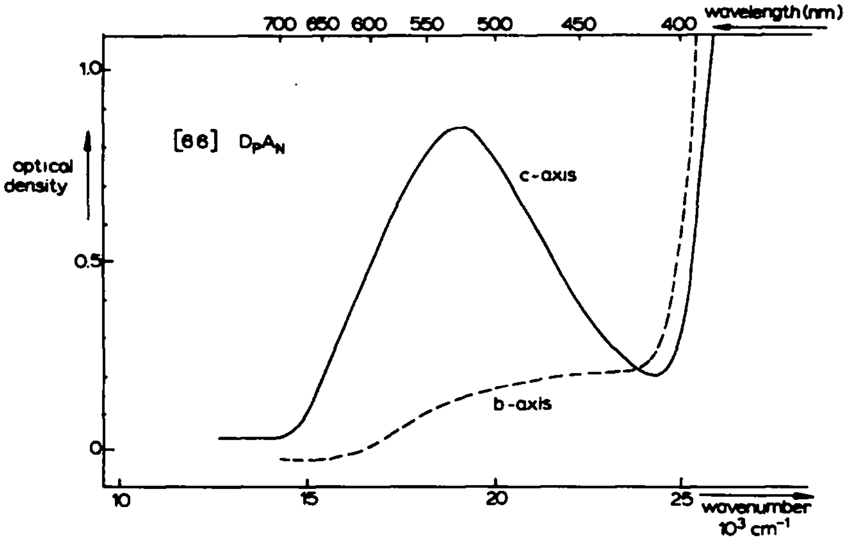


Fig. 3. Polarized absorption spectrum of [6.6]D$_p$A$_N$. The solid and dotted curves were obtained with the incident light polarized parallel to the crystallographic c- and b-axis respectively.

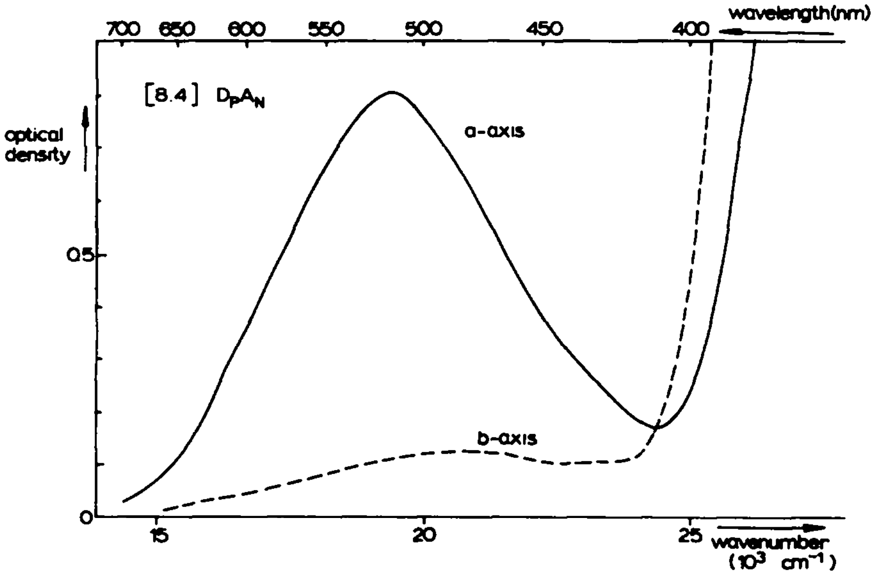


Fig. 4. Polarized absorption spectrum of [8.4]D$_p$A$_N$. The solid and dotted curves were obtained with the incident light polarized parallel to the crystallographic a- and b-axis respectively.

From an approximate measurement of the crystal thickness and with the known crystal densities the molar absorption coefficient of the CT-transition in the direction of maximum absorption was estimated as 175 and 255 $l.mol^{-1}.cm^{-1}$ (±50%) for [6.6]D_pA_N and [8.4]D_pA_N respectively. Thus the crystal spectra of both cyclophanes show a remarkable similarity both in intensity and in position of the CT transition notwithstanding the very different donor–acceptor orientations involved (see Fig. 2).

An interpretation of these results is hampered by the fact that, in the crystals, both intramolecular and intermolecular interactions may contribute to the absorptions observed. In order to estimate the relative importance of these effects, quantum mechanical calculations of the all-beta P.P.P. type were carried out for the various donor–acceptor orientations present in the crystal structure.

Calculations. It has been shown by Ohta *et al.*[16] as well as by other groups[17,18] that the electronic absorption spectra of π–π EDA complexes can be reproduced satisfactory by S.C.F.-MO-CI calculations of the P.P.P. type in which the complex is treated as a single conjugated system. In the present calculations the method of Ohta *et al.*[16] was adopted with slight simplifications.

Configuration interaction was limited to the lowest twenty five singly excited configurations and furthermore a different approach was used in calculating the overlap integrals $S_{\mu\nu}$ which are required to estimate the resonance integrals $\beta_{\mu\nu}$ when atoms μ and ν belong to different chromophores in the cyclophanes. In this case we used Cusachs–Corrington[19] AO's, which are easier to handle than the Clementi–Roothaan S.C.F.-AO's used by Ohta *et al.*, while their spatial distributions are known to be nearly equivalent at the distances involved in π–π complexation.

The present approach was found to yield results equivalent to those obtained by Ohta *et al.* when applied to a number of complexes for which both experimental and calculated CT spectra have been reported.[16]

The parameters used in the calculations of the cyclophanes are compiled in Table 3. These parameters were optimized to reproduce the absorption spectra of the separate donor and acceptor chromophores as measured for dilute dichloromethane solutions of 1,4 - dimethoxy - 2,5 - dimethylbenzene and N,N′ - di - n - butyl - 1,8:4,5 - naphthalene tetracarboxylic diimide respectively (see Table 4).

Calculations for the six donor–acceptor orientations present in the cyclophanes (see Fig. 2) were then performed. The results of these calculations for the first four electronic transitions are compiled in Table 5 together with the observed polarized absorption data.

The character of the transitions was investigated by calculating[16] the quantities $(DD)_m$, etc. as defined by (2)–(5). The CI wavefunction of the mth excited state being expressed by (1).

$$\psi_m = \sum_{(ij)} b_{ij,m}\varphi_{ij} \tag{1}$$

$$(DD)_m = \sum_{(ij)} b^2_{ij,m} D_i D_j \tag{2}$$

$$(AA)_m = \sum_{(ij)} b^2_{ij,m} A_i A_j \tag{3}$$

$$(DA)_m = \sum_{(ij)} b^2_{ij,m} D_i A_j \tag{4}$$

$$(AD)_m = \sum_{(ij)} b^2_{ij,m} A_i D_j. \tag{5}$$

In (1) $b_{ij,m}$ designates the coefficient of the singly excited configuration φ_{ij}, which corresponds to excitation from the MO level φ_i to φ_j. D_i and A_i give the weight of φ_i in donor and acceptor as obtained from (6) and (7), where n_d and n_a enumerate the atoms in D and A respectively,

Table 3. Semi empirical parameters used in the quantum mechanical calculations

Atom	H(X)	K(CX)	H_{ii}(eV)	γ_{ii}(eV)	C(eV)	S.E.	C.C.E.
C	0.0	1.0	10.50	11.13	14.50	1.625	0.880
C(αCH_3)	0.0	1.0	9.70	10.30	14.50	1.625	0.880
O-ether	2.0	0.8	34.00	21.40	45.00	2.450	1.220
N-imide	1.5	0.8	29.00	17.44	44.00	2.125	1.060
O-imide	1.0	1.6	18.90	14.40	29.00	2.275	1.220
C-imide	0.0	1.0	11.20	10.50	14.50	1.625	0.880

H(X)	Hückel Coulomb integral (β units)
K(HX)	Hückel bond integral (β units)
H_{ii}	One center core integral
γ_{ii}	One center repulsion integral
C	Penetration integral
S.E.	Slater-exponent
C.C.E.	Cusachs-Corrington-exponent

Table 4. Calculated and observed (dilute CH_2Cl_2 solution) electronic transitions for 1,4-dimethoxy-2,5-dimethylbenzene (D_p) and for N,N′-di-n-butyl-1,8:4,5-naphthalenetetracarboxylic diimide (A_N).

Chromophore	Calculated			Observed		
	ΔE (eV)	λ (nm)	f	ΔE (eV)	λ (nm)	f
Donor (D_p)	4.35	285	0.063	4.28	290	0.08
	5.42	229	0.240	5.51	225	0.29
Acceptor (A_N)	3.48	356	0.800	3.44	360	0.65
	3.59	345	0.158			
	5.19	239	0.656	5.21	238	0.63

while $c_{i\mu}$ gives the AO-coefficient of the atom μ in φ_i.

$$D_i = \sum_{\mu=1}^{n_d} c_{i\mu}^2 \tag{6}$$

$$A_i = \sum_{\mu=n_d+1}^{n_d+n_a} c_{i\mu}^2. \tag{7}$$

For all "complex" conformations the two longest wavelength transitions are calculated to be mainly CT (D→A) in character (see Table 5).

The calculated position of the first CT band coincides very well with the visible absorption maximum measured for the crystals. The extremely long wavelength calculated for [8.4]-inter-II forms an exception. It should be realized, however, that the geometrical parameters used for II are imprecise. Furthermore, the low population of II in the crystals probably means that the overall absorption measured for the crystals of [8.4]D_pA_N is mainly governed by molecules adopting conformation I.

The second CT transition is calculated to be situated rather close to the first strong acceptor transition which probably overshadows it in the experimental spectra. The third transition has mainly the character of a local excitation in A_N (LE(A^*)) and can be identified from its position and high intensity as related to the first transition of the isolated A_N chromophore (see Table 4).

It seems important to note that in all cases a certain mixing between this strong local A_N transition and the CT transitions is found, as evident from the characters given in Table 5. This mixing seems to account largely for the in-plane components of the CT transitions. The same arguments can qualitatively be applied to the fourth transition, which is also mainly LE(A^*) in character.

From the calculations it appears that for [6.6]D_pA_N the intermolecular interaction contributes predominantly to the visible absorption of the crystals. The calculated total oscillator strength (inter + intramolecular) along the c-axis ($f_c = 0.0145$) is higher than that observed experimentally ($f_c = 0.004$) while the calculated polarization ratio $f_c/f_b = 5.6$ agrees very well with the experimental ratio ($f_c/f_b = 4.3$).

For [8.4]D_pA_N the calculations predict that the intramolecular interactions (especially those in I) contribute predominantly to the visible absorption of the crystals. The calculated total f_a (weighted for I/II = 4) amounts to $f_a = 0.048$ which is larger than the experimental value ($f_a = 0.006$), while again the calculated polarization ratio $f_a/f_b = 6.5$ agrees quite well with the experimental value $f_a/f_b = 8$.

A part of the discrepancy between the observed and the calculated oscillator strengths is due to the uncertainty in the experimental result. A major part, however, can be ascribed to the shortcomings of our theoretical model. There is computational[20] and analytic[21] evidence to show that the consideration of both doubly excited π-configurations and the polarisability of the σ-frame tends to result in a lowering of the transition probabilities.

Moreover, the method used for the calculation of the intermoiety $\beta_{\mu\nu}$ should be reconsidered. If we switch for a moment to a description of the complex in terms of the MO's of its components D and A, then the zero order approximation of the charge transfer excitation reads $DA + \lambda D^+A^- \rightarrow D^+A^- - \lambda DA$, and it is readily derived that in the same approximation the transition probability is given by

$$\langle r \rangle \approx \sum_{\mu}\sum_{\nu} c_{i\mu} c_{j\nu} \beta_{\mu\nu} \tag{8}$$

where $c_{i\mu}$ and $c_{j\nu}$ are the expansion coefficients of the highest occupied donor and lowest unoccupied acceptor M.O.'s. It follows from (8) that a systematic lowering of $\beta_{\mu\nu}$ will strongly affect the oscillator strength, which is proportional to $\langle r \rangle^2$.

In our calculation we used the assumption of Ohta *et al.*[16] that $\beta_{\mu\nu}$ is proportional with the overlap integral S:

$$\beta_{\mu\nu} = c_{\mu\nu} S_{\mu\nu}. \tag{9}$$

This assumption, however, may be seriously wrong. According to a recent analysis[22] $\beta_{\mu\nu}$ cannot be correctly described in terms of μ and ν alone: if the mutual orthogonalisation of all atomic orbitals is taken into account it can be shown that $\beta_{\mu\nu}$ depends critically on the position and the nature of *all* atoms near the $\mu\nu$-bond. Indeed, if a third atom is close to the centre of the bond (which is the case with second neighbours in a molecule) then the β-value obtained from (9) is too large by an order of magnitude. In the case of the cyclophanes, where the lines connecting μ and ν with their neighbours in D and A are roughly perpendicular to the $\mu\nu$-bond, a simple model calculation according to[22] suggests that the leading terms found from (8) and (9) are too high by a factor of about 2.

Though an accurate calculation of f cannot be performed, there is ample evidence to show that the simplifications inherent to our model must result in calculated f-values that are considerably larger than the experimental ones.

Table 5. Calculated and observed spectroscopic data for crystals of [6.6]D_pA_N and [8.4]D_pA_N

System	Conformation	Transition	Calculated											Observed
			Position		Oscillator strength				Character of transition				Assignment	
			eV	nm	f	f_a	f_b	f_c	$(DD)_m$	$(AA)_m$	$(DA)_m$	$(AD)_m$		
[6.6]	intra	1	2.38	521	0.0124	0.0054	0.0009	0.0043	0.001	0.022	0.976	0.000	CT(D-A)	525 nm (2.34 eV) f_c = 0.004 f_c/f_b = 4.3
		2	3.29	377	0.0297	0.0082	0.0217	0.0007	0.001	0.088	0.911	0.000	CT(D-A)	
		3	3.50	354	0.6895	0.3764	0.3243	0.0138	0.000	0.970	0.029	0.001	LE(A•)	
		4	3.57	347	0.2486	0.0100	0.2387	0.0001	0.000	0.951	0.049	0.000	LE(A•)	
	inter	1	2.30	538	0.0170	0.0084	0.0017	0.0102	0.004	0.041	0.956	0.000	CT(D-A)	
		2	2.84	437	0.1072	0.1067	0.0024	0.0004	0.003	0.289	0.707	0.001	CT(D-A)+LE(A•)	
		3	3.49	355	0.6870	0.1364	0.5543	0.0032	0.001	0.891	0.105	0.004	LE(A•)+CT(D-A)	
		4	3.92	316	0.0828	0.0723	0.0127	0.0021	0.001	0.447	0.551	0.002	LE(A•)+CT(D-A)	
[8.4]	intra I	1	2.32	534	0.0749	0.0474	0.0068	0.0207	0.007	0.050	0.943	0.000	CT(D-A)	515 nm (2.41 eV) f_a = 0.006 f_a/f_b = 8
		2	3.14	394	0.1466	0.0118	0.0059	0.1289	0.006	0.186	0.806	0.001	CT(D-A)+LE(A•)	
		3	3.58	347	0.5539	0.0123	0.2914	0.2502	0.001	0.877	0.117	0.006	LE(A•)+CT(D-A)	
		4	3.64	341	0.2096	0.0020	0.0046	0.2030	0.001	0.960	0.133	0.006	LE(A•)+CT(D-A)	
	inter I	1	2.30	539	0.0053	0.0007	0.0019	0.0027	0.003	0.025	0.972	0.000	CT(D-A)	
		2	2.85	435	0.1500	0.0052	0.0018	0.1430	0.002	0.292	0.703	0.001	CT(D-A)+LE(A•)	
		3	3.49	355	0.4765	0.0291	0.2935	0.1539	0.000	0.849	0.147	0.003	LE(A•)+CT(D-A)	
		4	3.83	324	0.3192	0.0003	0.0127	0.3062	0.000	0.852	0.144	0.003	LE(A•)+CT(D-A	
	intra II	1	2.33	533	0.0712	0.0378	0.0017	0.0317	0.006	0.040	0.953	0.000	CT(D-A)	
		2	3.17	391	0.0962	0.0185	0.0510	0.0267	0.005	0.167	0.826	0.001	CT(D-A)+LE(A•	
		3	3.56	348	0.6900	0.0086	0.1809	0.5005	0.000	0.912	0.080	0.005	LE(A•)	
		4	3.63	341	0.1348	0.0031	0.0772	0.0545	0.001	0.879	0.114	0.005	LE(A•)+CT(D-A	
	inter II	1	2.11	588	0.0590	0.0101	0.0002	0.0487	0.003	0.109	0.887	0.000	CT(D-A)+LE(A•)	
		2	3.08	403	0.0805	0.0052	0.0296	0.0457	0.003	0.135	0.862	0.000	CT(D-A)+LE(A•)	
		3	3.50	354	0.2934	0.0193	0.2091	0.0650	0.000	0.818	0.179	0.002	LE(A•)+CT(D-A)	
		4	3.71	334	0.3599	0.0013	0.0345	0.3241	0.001	0.602	0.395	0.002	LE(A•)+CT(D-A)	

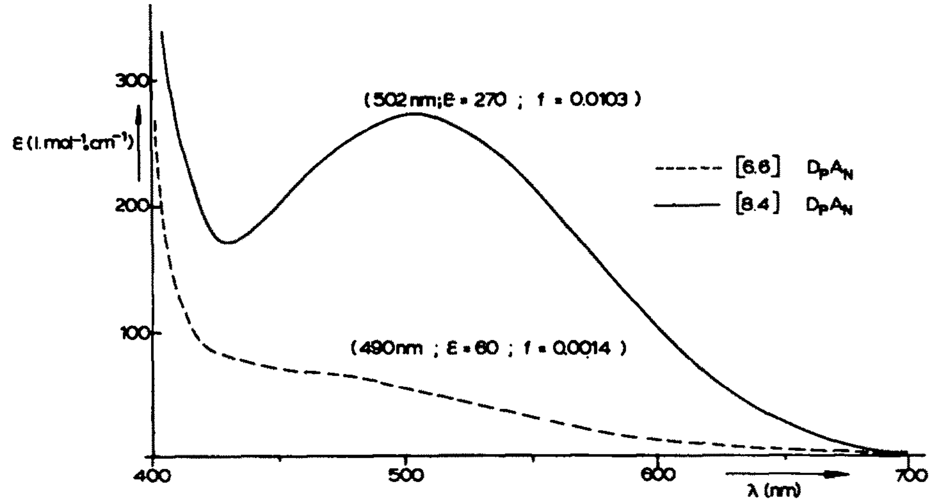


Fig. 5. Long wavelength absorption spectra of $[6.6]D_pA_N$ and $[8.4]D_pA_N$ in dilute (10^{-3} M) dichloromethane solution.

Concluding remarks. From a comparison of the experimental data and the quantum mechanical calculations it appears that the remarkable similarity in the visible absorption of the crystals of both cyclophanes is mainly due to the simultaneous occurrence of inter- and intramolecular donor–acceptor interactions in the solid state.

This interpretation is supported by the observation that in dilute solution the visible absorption of these compounds differs widely in intensity (see Fig. 5). By far the strongest absorption is found for $[8.4]D_pA_N$ which seems to agree with the conclusion, that for this compound intramolecular interaction is dominant.

It should be realized however, that the conformation of these rather flexible cyclophanes in solution is not necessarily identical to that found in the crystals. Further studies on the implications of conformational mobility of EDA cyclophanes in solution are in progress and will be reported separately.

EXPERIMENTAL

Materials. Syntheses and structure determination of the compounds have been described elsewhere.[2,7]

Spectra. Solution phase absorption spectra were obtained with a Cary 17D recording spectrophotometer using CH_2Cl_2 (Merck, UV-grade) as a solvent.

Polarized absorption spectra were obtained with an Olympus Microspectrophotometer.[2,3] The measurements were made on thin rectangular crystal plates. The thickness of the plates was determined by focussing a microscope, fitted with calibrated focus adjustment, onto top and bottom crystal faces and was found to be 2×10^{-3} cm for $[6.6]D_pA_N$ and 1.5×10^{-3} cm for $[8.4]D_pA_N$.

For $[6.6]D_pA_N$ the elongated and short sides of plates corresponded to the directions of the crystallographic c- and b-axes respectively and for $[8.4]D_pA_N$ to the directions of the a- and b-axes respectively.

Calculations were performed on the Cyber 73-26 computer of the academic computing center in Amsterdam (SARA).

Acknowledgements—The present investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We thank the Royal Society for the award of an Overseas Fellowship (to J.D.W.) under its Japan exchange programme, and Dr. S. de Bruijn for his valuable discussion of the quantum mechanical calculations. We are much indebted to Drs. A. R. Overbeek, Dr. C. H. Stam and Dr. H. Schenk who made the crystallographic data available[15] prior to publication.

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