Table I. Atomic Parameters for 1,4-Cyclohexadiene at 153 K[a]

atom	x	y	z	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.1182 (2)	0.4113 (2)	0.9059 (1)	3.57 (8)	4.04 (8)	4.07 (8)	−0.05 (7)	0.21 (6)	−0.83 (6)
C(2)	0.0082 (2)	0.5470 (2)	0.8626 (1)	4.17 (8)	4.55 (8)	3.39 (8)	−0.43 (7)	−0.21 (7)	0.13 (6)
C(3)	0.1227 (2)	0.3472 (2)	1.0485 (2)	4.02 (9)	4.43 (9)	4.86 (9)	0.77 (8)	−0.46 (7)	0.21 (7)
H(1)	0.199 (2)	0.346 (2)	0.845 (1)	4.6 (4)					
H(2)	0.006 (2)	0.581 (2)	0.765 (2)	5.4 (4)					
H(3)	0.094 (2)	0.211 (2)	1.054 (1)	6.8 (5)					
H(4)	0.253 (2)	0.352 (2)	1.079 (1)	5.4 (4)					

[a] U_{ij} and U in Å^2 × 100. The temperature factors are of the following form: $T(\text{aniso}) = \exp(-2\pi^2\{U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*\})$; $T(\text{iso}) = \exp(-8\pi^2U\sin^2\theta/\lambda^2)$.

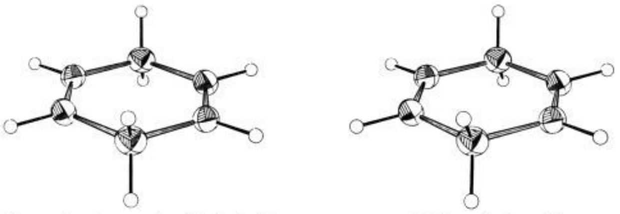

Figure 1. Stereoview[22] of the X-ray structure of 1,4-cyclohexadiene at 153 K. Thermal ellipsoids are drawn at 50% probability.

evidence for the planar structure. An early molecular mechanics calculation[8] favored an averaged structure across a shallow boat-boat inversion potential. Two later ab initio molecular orbital calculations predicted a planar structure with a shallow potential in the direction of the boat distortions.[15,16]

We have determined the crystal structure of C_6H_8, mp 223 K, at 153 K. Crystallization was at 200 K directly on the X-ray diffractometer using a procedure described elsewhere.[17] While cooling down no phase transition was observed, though expected to be at 193 K as a previously taken DTA suggested. Further attempts to obtain the low-temperature phase were not successful. The crystal structure is orthorhombic, *Pbca* with four molecules in the unit cell (as for benzene[18]). In the absence of disorder, the molecular symmetry is required to be $\bar{1}$, which is a planar or chair ring conformation. The diffraction data were collected at 153 K on a crystal of the supercooled high-temperature form. The intensities of 444 unique reflections, of which 31 had $|F_o| < 2\sigma$, were measured with Zr-filtered Mo Kα radiation. The unit cell dimensions at 153 K are a = 7.070 (3), b = 7.169 (2), and c = 9.909 (2) Å. The structure was solved by using SHELXS-86,[19] and the parameters were refined by using XTAL[20] to disagreement factors of $R = 0.037$, $R_w = 0.034$ ($w = \sigma(F_o)^{-1}$) for 44 parameters. The final difference maps showed no peaks greater than 0.15 eÅ^{-3}. The atomic parameters are given in Table I.

The carbon atom ring is planar within 0.002 Å (see Figure 1). The root-mean-square displacements of the carbon atoms perpendicular to the plane of the molecule, calculated from the anisotropic thermal motion tensors, are C(3) 0.22 (3), C(1) 0.19 (3), and C(2) 0.20 (3) Å. Although that of C(3) is longer than for C(1) and C(2), the differences are not significant. There is therefore no evidence of any disorder involving a boat, or chair, conformation. However, it is important to remark that disorder involving very small distortions from planarity can never be excluded by means of a crystal structure analysis at one temperature.

The C–C bond lengths and angles are compared with those reported from the other studies in Table II. The C–H bond lengths are 0.95 to 1.00 Å, with H–C(3)–H = 103 (1)°.

Table II. Bond Lengths and Valence Angles in 1,4-Cyclohexadiene

	this work[a]	electron diffrctn[b]	electron diffrctn[c]	ab initio MO[d]	ab initio MO[e]
C(1)=C(2)	1.318 (2)	1.347 (4)	1.334 (2)	1.309 (1.339)	1.317
C(1)–C(3′)	1.486 (2)	1.511 (4)	1.496 (1)	1.522	1.509
C(2)–C(3)	1.486 (2)			(1.511)	
C(1)–C(3′)–C(2′)	113.1 (1)	(111.9)	113.3 (3)	112.3	112.4
C(1)–C(2)–C(3′)	123.5 (1)	122.7 (3)			
C(3′)–C(1)–C(2)	123.4 (1)		123.4 (6)	120.4	123.8

[a] Uncorrected for thermal motion, estimated corrections +0.005 Å.[18] Distances in Å, angles in deg. [b] Reference 6. [c] Reference 3. [d] Using GAUSSIAN with STO-3G.[15] The values in parentheses are corrected from STO-3G to MP2/6-31G* by the offset method using C–C in C_2H_6 and C=C in C_2H_4.[21] [e] Using MOLECUL with (7,3) → (4,2) for C, (4) → (2) for H.[16]

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Supplementary Material Available: List of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Achieving High Quantum Yield Charge Separation in Porphyrin-Containing Donor–Acceptor Molecules at 10 K

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A long-standing problem in the study of porphyrin- and chlorophyll-based donor–acceptor compounds designed to mimic photosynthesis is the failure of most of these molecules to undergo high quantum efficiency photoinitiated charge separation in the solid state at very low temperatures.[1] The rate constants for oxidation of the lowest excited singlet states of porphyrin donors by acceptors decrease sharply at the freezing points of the media in which the compounds are dissolved.[1] This results in a small or negligible quantum yield of charge separation because the rate of electron transfer cannot compete with the decay of the porphyrin excited singlet state to ground state. This behavior contrasts sharply with the slight increase in rate for primary electron transfer exhibited by photosynthetic reaction centers upon cooling to 4.2

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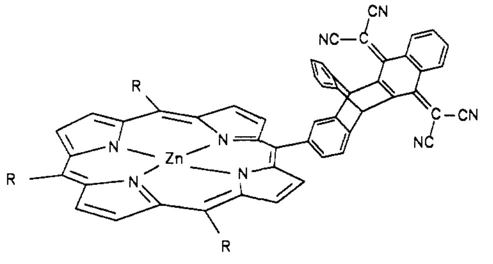
Table I. Energetics (eV)

compd	$E^{+}_{1/2}$[a]	$E^{-}_{1/2}$[a]	$-\Delta G_{cs}$	$-\Delta G_{cr}$	S_1	T_1
1	0.80	0.05	1.32	0.75	2.07	1.58[b]
2	0.61	0.05	1.49	0.56	2.05	1.55[c]
ZnTPP	0.80				2.07	1.58[b]
Zn-tripentylmonophenylporphine	0.61				2.05	1.55[b]
triptycene–TCNQ		0.05				

[a] Reversible half-wave potentials determined at 294 K in MTHF containing 0.1 M n-$Bu_4N^+BF^-_4$; Pt disc working electrode; SCE reference electrode. $-\Delta G_{cs}$ = free energy of charge separation. $-\Delta G_{cr}$ = free energy of charge recombination. [b] Triplet energies were determined from the energy of the (0,0) band in the phosphorescence spectra of the Zn porphyrins at 77 K. [c] Estimated from the triplet energy of Zn-tripentylmonophenylporphine.

K.[2] In low-temperature solid solutions dipole rotations of the solvent are eliminated as a source of stabilization of the incipient ion pair. Thus, the ion pair energy is increased, the free energy of the charge separation reaction is less negative, and the reaction rate is slower.[3]

In order to study the rates and energetics of these electron-transfer reactions at very low temperatures we have prepared two new fixed-distance donor–acceptor molecules, **1** and **2**.[4] The donors are Zn porphyrins, and the acceptor is a high electron affinity tetracyanonaphthoquinodimethane (TCNQD) derivative. By design compounds **1** and **2** possess very large negative free energies for charge separation at 294 K, Table I. Thus, the energy of the ZnP^+–$TCNQD^-$ ion pair at 10 K should remain below that of the lowest excited singlet state of the Zn porphyrin, even if ZnP^+–$TCNQD^-$ is considerably destabilized relative to its energy at 294 K.



1: R = phenyl; 2: R = n–pentyl

All measurements of the properties of **1** and **2** were carried out in 2-methyltetrahydrofuran (MTHF). The ground-state absorption spectra of **1** and **2** are essentially a superposition of the spectra of the individual chromophores, which indicates that the ground-state interactions between the donors and the acceptors are weak. However, the fluorescence quantum yields for the Zn porphyrins in both **1** and **2** are <0.0001 at both 294 and 10 K.[5] Since the fluorescence quantum yields of Zn *meso*-tetraphenylporphine (ZnTPP)[6] and Zn *meso*-tripentylphenylporphine ($ZnPn_3PP$) are both about 0.03, the fluorescence quenching in **1** and **2** suggests that a >99% efficient nonradiative decay pathway exists in **1** and **2**. Transient absorption spectra of **1** and **2** at 10 K following excitation with a 1 ps laser pulse at 610 nm[7] show that this pathway is oxidation of the lowest excited singlet state of the Zn-porphyrins by the TCNQD acceptor to yield ZnP^+–$TCNQD^-$, Figure 1. The spectra at 10 ps can be clearly ascribed to formation of the ZnP^+–$TCNQD^-$ radical ion pair, since the absorbances near 460 nm, and more distinctly, from 650–750 nm, are due to ZnP^+.[8] The transient absorption for **1** at 700 nm appears with τ = 2.2 ps and decays with τ = 520 ps, while that of **2** appears with τ = 2.4 ps and decays with τ = 280 ps.[9] On the other hand, at 294 K the radical ion pairs of **1** and **2** are formed within the 1 ps resolution of the instrument and decay to ground state with τ = 2.9 and 2.6 ps, respectively. The rate constants for both the charge separation and ion pair recombination reactions of **1** and **2** decrease rapidly and reach their lower limit between 150 and 100 K, as the viscosity of MTHF increases sharply when it forms a glassy solid. Even though the radical ion pair lifetimes for **1** and **2** are much longer at 10 K than at 294 K, the charge separation rate constants remain large, and the quantum yields of charge separation remain essentially unity at both temperatures.

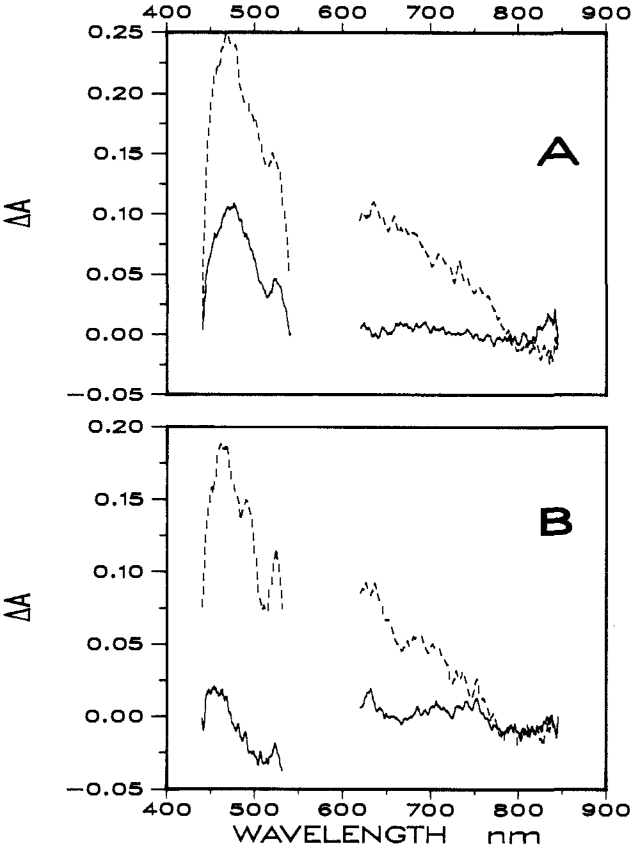


Figure 1. Transient absorption spectra obtained 10 ps (– –) and 1 ns (—) following a 1 ps, 610 nm, 0.4 mJ laser flash for **1** (A) and for **2** (B). Filters that reject stray excitation light cut out the 540–620-nm region, while the sharp cutoff at 440 nm is due to the intense absorption of the Soret band at 419 nm.

The transient absorption changes at 10 K show that the radical ion pair of **1** decays to a longer lived species that absorbs strongly near 470 nm and weakly near 845 nm, Figure 1, while that of **2** decays almost completely to ground state. The spectrum of the longer lived state of **1**, which is produced following radical ion pair recombination, matches that of the lowest excited triplet state of ZnTPP.[10]

EPR spectroscopy of **1** in MTHF at 10 K provides further evidence of triplet formation. Figure 2 shows the EPR powder spectra for the triplet states of ZnTPP and **1**.[11] ZnTPP exhibits a triplet EPR spectrum with a spin polarization pattern (aaa eee)[12] which shows that the triplet state is derived from the singlet by

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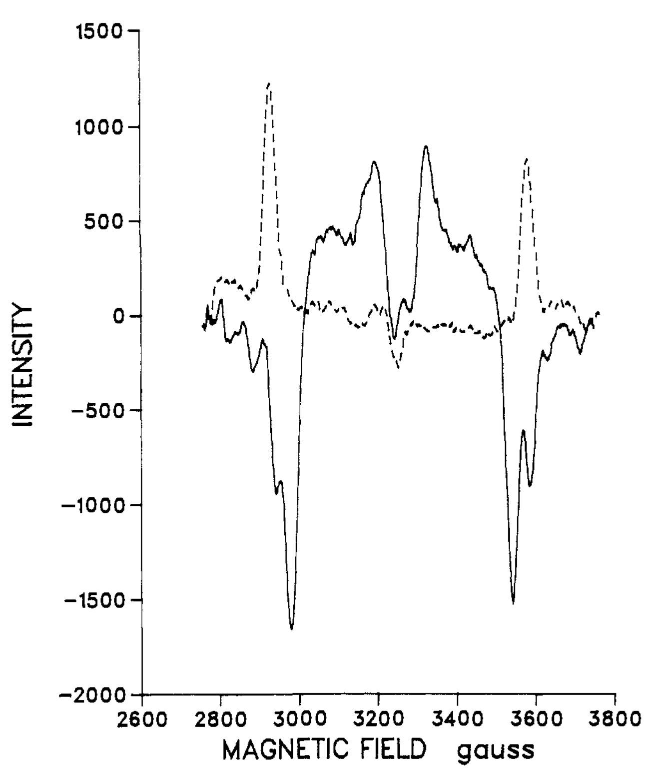

Figure 2. EPR powder spectra of the lowest excited triplet states of ZnTPP (--) and **1** (—) at 10 K in MTHF. Positive signals are in absorption, and negative signals are in emission. The zero-field splitting parameters for ZnTPP and **1** are, respectively, $|D|$ = 0.0305 and 0.0300 cm^{-1}, $|E|$ = 0.0085 and 0.0080 cm^{-1}.

spin-orbit induced intersystem crossing primarily to the z sublevel of the triplet state. This is typical of Zn containing porphyrins and chlorophylls.[13] The z-direction in the principal magnetic axis system for porphyrin π–π^* triplet states is normal to the plane of the macrocycle. In strong contrast to ZnTPP, **1** shows an intense triplet EPR signal possessing a spin polarization pattern (eea eaa) which shows that an in-plane sublevel of the triplet state is overpopulated.[12] Thus, the triplet state of **1** is not formed via the usual intersystem crossing mechanism for Zn porphyrins. Singlet radical ion pairs in covalently linked donor–acceptor molecules can undergo subnanosecond intersystem crossing leading to triplet formation.[14] Intersystem crossing rates are enhanced by a spin-orbit interaction when the symmetry axes of the donor HOMO and the acceptor LUMO lie between 45° and 90° relative to one another. The π systems of the donor and acceptor in **1** and **2** lie about 60° relative to one another.[15] Since the electron acceptor lies approximately on the inplane symmetry axis of the porphyrin, rapid intersystem crossing preceding ion pair recombination produces a triplet state in which an in-plane sublevel of the porphyrin is overpopulated. On the other hand, *no triplet EPR signal is observed for **2***. This result agrees with the optical transient absorption data which show that excitation of **2** yields little or no triplet Zn-porphyrin.

The optical and EPR results at 10 K suggest that the radical ion pair state of **1** is above the triplet state of its Zn-porphyrin, while that of **2** is below the triplet state of its Zn-porphyrin. Thus, we can estimate the change in the radical ion pair energy that occurs when the solvent is frozen to a solid at low temperature. Since the energies of the lowest excited triplet states of the porphyrins in **1** and **2** are about 1.58 and 1.55 eV, respectively, and since the energies of the radical ion pairs for **1** and **2** at 294 K in fluid solution are about 0.75 and 0.56 eV, respectively, the increase in radical ion pair energy is 0.99 eV > ΔG > 0.83 eV or about 0.9 eV. Thus, the fact that most porphyrin-based donor–acceptor molecules exhibit very low quantum yields for charge separation in low-temperature solids results in a large part from destabilization of the ion pair state in low-temperature solids relative to polar liquids. These experiments permit us to begin to study more closely the role of the medium in electron-transfer reactions and may allow us to understand the behavior of photosynthetic reaction centers at low temperature.

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Supplementary Material Available: Synthesis information for **1** and **2** (2 pages). Ordering information is given on any current masthead page.

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Solid-State NMR Detection of Proton Exchange between the Bacteriorhodopsin Schiff Base and Bulk Water

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Liquid-phase NMR has been employed extensively to investigate the rates and mechanisms of chemical reactions, particularly exchange reactions at equilibrium.[1,2] By monitoring the dynamics of either longitudinal[3] or transverse magnetization,[4] in one- and/or two-dimensional NMR[5] experiments, one can usefully measure

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