the primary photoisomerization step is responsible for the finely tuned light-sensing mechanism of phytochrome. The molar absorptivities of native Pr and Pfr phytochromes are very similar (Figure 2), though the molar absorptivities of their free chromophores differ markedly. The proposed model provides for a photoreceptor that is equally sensitive to both red and far-red light and can thus respond equally well to fluctuations in the light environment of plants.

More detailed analysis of the SERRS spectra is required, along with use of different wavelength excitations. Work of this type is now in progress in this laboratory.

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Conformational Analysis. 13. Molecular Structure and Conformation of 2-Bromopropenal As Determined by Gas-Phase Electron Diffraction

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Abstract: 2-Bromopropenal has been studied by gas-phase electron diffraction at 353 K. Two conformers were identified, a more stable planar anti form and a less stable planar (or near-planar) syn form. The mole fraction of the anti form, with uncertainty estimated at 2σ, was found to be 0.64 (11). Assuming the two conformers to have equal entropy, this corresponds to an energy difference of $\Delta E^\circ = E_s^\circ - E_a^\circ = 1.7 \pm 1.4$ kJ·mol^{-1}. Values of bond distances (r_a) and valence angles ($\angle_\alpha$) with estimated 2σ uncertainties are the following: r(C—H) = 1.103 (28) Å, r(C=O) = 1.219 (8) Å, r(C=C) = 1.350 (13) Å, r(C—C) = 1.498 (13) Å, r(C—Br) = 1.883 (8) Å, ∠C—C=C = 121.7 (11)°, ∠C—C=O = 124.0 (17)°, ∠C—C—Br = 116.1 (19)°, ∠C=C—H = 122 (9)°, ∠C—C—H = 115 (10)°, σ_{anti} (root mean square torsional amplitude for the anti conformer) = 25 (10)°, σ_{syn} = 27 (14)°.

Most molecules with a conjugated diene system have been found to have the double bonds anti to each other. For several such compounds, an additional form has also been observed where the double bonds are either syn or gauche to each other. Propenal[1,2] (CH_2=CH—CH=O) and glyoxal[2] (O=CH—CH=O) are mixtures of anti and syn conformers, while oxalyl chloride[3] and oxalyl bromide[4] (O=CX—CX=O, X = Cl, Br) both have a nonplanar gauche form in addition to the anti conformer. In propenoyl chloride[5] (CH_2=CH—CCl=O) and 2-chloropropenoyl chloride[6] (CH_2=CCl—CCl=O) the low-energy conformer is again the planar anti form, while the second conformer is a planar, or very nearly planar, syn form. The energy difference between the conformers is found to be reduced when an aldehyde proton is replaced by a halogen atom.

In order to further determine the conformational effects of different substituents in molecules like these, we were also interested in studying propenals substituted with a halogen atom in the 2-position. We therefore initiated an electron diffraction investigation of 2-bromopropenal (Figure 1). The results for 2-chloropropenal have since then also been published,[7] and a mixture of conformers was observed, anti with a planar or nearly planar molecule and gauche with a torsion angle of $\phi = 136 \pm 8°$ ($\phi = 0°$ for a planar anti form).

Experimental and Data Reduction

2-Bromopropenal was prepared as described by Berlande.[8] The sample was purified by several vacuum destillations and stored at −78 °C in the dark. Electron diffraction photographs were recorded at 353 K with the Oslo Balzers instrument[9,10] on Kodak electron image plates. The voltage/distance calibration was made with benzene as reference. The nozzle-to-plate distances were 500.12 and 250.12 mm for the long and the short camera experiments and the electron wavelength was 0.05864 Å. Three plates from the long and five plates from the short camera distances were selected for analysis. Optical densities were measured using a Joyce Loeble double-beam microdensitometer and the data were reduced in a way reported elsewhere.[3,11-13] The data covered the range $2.00 \leq s \leq 14.75$ Å^{-1} and $4.00 \leq s \leq 25.00$ Å^{-1} ($s = 4\pi\lambda^{-1} \sin \theta$, where λ is the electron wavelength and 2θ is the scattering angle), and the data interval was $\Delta s = 0.25$ Å^{-1}. The average experimental intensity curves in the form of $sI_m(s)$ are shown in Figure 2; data for the individual curves and backgrounds[13] are available as supplementary material. The atomic scattering and phase factors used were obtained from the tables of Schäfer et al.[14]

Structure Analysis

An experimental radial distribution (RD) curve (Figure 3) was calculated in the usual way by Fourier transformation of the function $I'(s) = sI_m(s)Z_cZ_{Br}A_c^{-1}A_{Br}^{-1} \exp(-Bs^2)$ with $B = 0.0020$ Å^2. The A's are electron scattering amplitudes multiplied by s^2. Data for the unobserved region $0 \leq s \leq 1.75$ Å^{-1} were at first omitted and in later calculations taken from models close to the final one.

The appearance of the radial distribution curves (the final ones are shown in Figure 3) led to trial values for the important bond distances and valence angles. These values agreed quite well with the results reported for related molecules. The experimental RD

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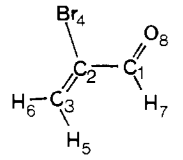

Figure 1. Molecular model of the anti (ϕ = 0°) conformer of 2-bromopropenal showing the atomic numbering.

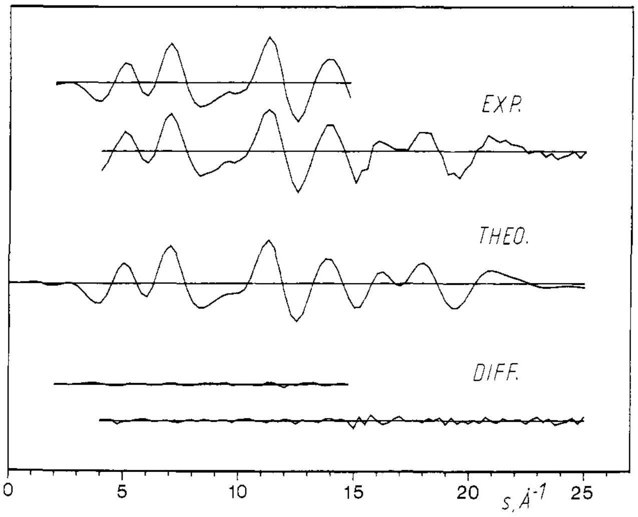

Figure 2. Average experimental intensity curves for 2-bromopropenal shown together with the theoretical curve calculated from the parameter values of Table I.

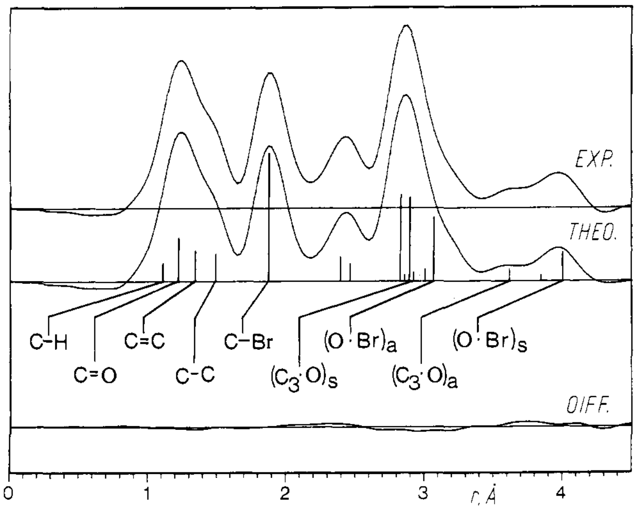

Figure 3. Radial distribution curves calculated from the curves of Figure 2. The vertical lines indicate the most important interatomic distances; their lengths are proportional to the weights of the distances.

curve also revealed that the sample contained more than one conformer. The longest main distance in a planar anti form is the $C_3 \cdots O$ distance at approximately 3.6 Å. The experimental curve showed a peak at this point, but the area under this peak was too small to correspond to 100% of the anti form. We also observed a large peak in the experimental curve at approximately 4.0 Å, and calculations of theoretical RD curves (Figure 4) showed that this was due to the long O···Br distance in a second conformer. From the position of this peak it was clear that this conformer had to be planar or nearly planar, and from the relative area of the two peaks at 3.6 and 4.0 Å, it was estimated that approximately 35% of the molecules had the syn form.

Refinements of the structure were carried out by the method of least squares based on intensity curves,[15] adjusting a single theoretical curve to the two experimental curves (one from each of the two nozzle-to-plate distances), using a unit weight matrix. We first assumed that the two conformers differed only in the C=C—C=O torsion angle. Later we also tested the effect of allowing some of the valence angles to have different values in the two forms, but this led to no significant improvement in the fit between experimental and theoretical curves. Assuming the two C=C—H angles to be equal, the geometry of 2-bromopropenal can be described by the 12 parameters r(C—H), r(C=O), r(C=C), r(C—C), r(C—Br), ∠C=C—C, ∠C=C—H, ∠C—C—H, ∠C—C=O, ∠C—C—Br, ϕ_a, and ϕ_s where ϕ_a and ϕ_s are the C=C—C=O torsion angles in the anti and syn conformers, respectively. Later, dynamic models were introduced where each conformer was represented by five torsional pseudoconformers as described earlier.[3,5] Conversion of the structurally consistent set of r_α distances for the molecule to r_a for use in the scattered intensity formula was done in a similar way to that described for propenoyl chloride.[5] No vibrational frequencies have been reported for 2-bromopropenal, and we therefore used the force field developed for similar molecules[5,16] with the necessary modification for the bromine substitution. Tables of the symmetry coordinates and the force constant values are available in the supplementary material. Vibrational amplitudes were also calculated from this force field and calculated values were used for those amplitudes not being refined in the least-squares analysis.

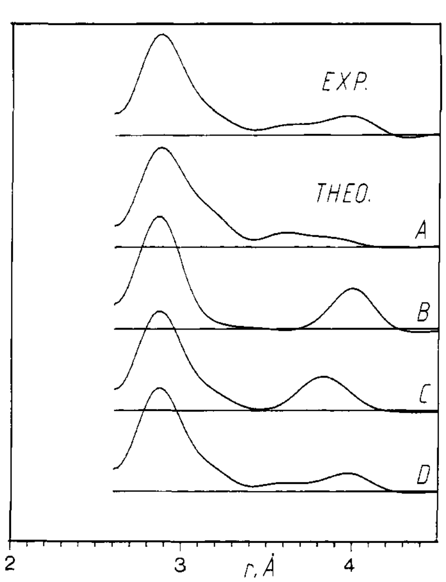

Figure 4. Theoretical radial distribution curves for anti (A), syn (B), or gauche (C) conformers, and for a mixture of 64% anti and 36% syn (D), together with the experimental curve. Only the conformationally important parts of the curves are shown.

The equilibrium values for the C=C—C=O torsion angle in the two forms were difficult to determine with certainty, and several different models were tested. If we assumed no large-amplitude torsional motion, the values obtained for the C=C—C=O angle were ϕ_a = 18 ± 14° and ϕ_s = 156 ± 12° (ϕ = 0° for a planar anti conformer). However, these values are typical for a planar molecule undergoing large-amplitude torsional motion, and introducing a dynamic model we got slightly improved fit between experimental and theoretical data with root-mean-square (rms) torsional amplitudes σ_a = 25 ± 10° and σ_s = 27 ± 14°. It is also possible to construct a dynamic model with a "hump" in the potential at the planar syn position and, with low values for the height of this barrier ($V_0 < 2$ kJ), this model gave almost as good a fit to the experimental data as the other dynamic model. The same was also found for 2-chloropropenoyl chloride.[6] Fortunately, the choice of torsional model did not have any effect on the geometrical parameter values, and we have chosen to present the results for the dynamic modell with planar equilibrium values for ϕ as our final results. They are shown in Table I, and

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Table I. Final Parameter Values for 2-Bromopropenal

parameter[a]		$r_a/\angle\alpha$	l
r(C—H)		1.103 (28)	0.077
r(C=O)		1.219 (8)	0.039
r(C=C)		1.350 (13)	0.044
r(C—C)		1.498 (13)	0.050
r(C—Br)		1.883 (8)	0.057 (13)
∠C—C=C		121.7 (11)	
∠C—C=O		124.0 (17)	
∠C—C—Br		116.1 (19)	
∠C=C—H		122 (9)	
∠C—C—H		115 (10)	
σ_a[b]		25 (10)	
σ_s[b]		27 (14)	
% anti		64 (11)	
		Selected Dependent Distances	
$r(C_2\cdot O)$		2.402 (14)	0.064
$r(C_1\cdot C_3)$		2.483 (8)	0.068
$r(C_3\cdot Br)$		2.838 (24)	0.072
$r(C_1\cdot Br)$		2.874 (31)	0.075
$r(H_6\cdot Br)$		3.015 (56)	0.162
$r(H_5\cdot Br)$		3.864 (17)	0.104
$r(O\cdot Br)$	anti	3.081 (25)	0.116
$r(O\cdot C_3)$		3.613 (14)	0.070
$r(H_7\cdot Br)$		3.857 (50)	0.102
$r(O\cdot Br)$	syn	4.039 (16)	0.075
$r(O\cdot C_3)$		2.886 (30)	0.107
$r(H_7\cdot Br)$		2.864 (187)	0.142

[a] Distances (r_a) and vibrational amplitudes are in ångströms; angles ($\angle_\alpha$) are in degrees. Parenthesized values are 2σ and include estimates of the uncertainty in voltage/nozzle heights and of correlation in the experimental data. [b] σ_s and σ_s are the rms torsional amplitudes in degrees for the anti and syn conformers, respectively.

the theoretical intensity and RD curves corresponding to these results are shown in Figures 2 and 3 together with difference curves. The correlation matrix is given in Table II.

Discussion

Our results for 2-bromopropenal showed a mixture of substantial amounts of two planar, or very nearly planar conformers. This is in agreement with the results found for propenoyl chloride[5] and 2-chloropropenoyl chloride.[6] For propenal itself two planar forms have also been found, but here the energy difference between the two forms is large enough to make the anti conformer the major form. Substituting a hydrogen atom with an electronegative halogen atom therefore clearly reduces the energy difference between the syn and the anti conformers in molecules like these. A reduction in energy difference was also observed for 2-chloropropenal[7] compared with propenal,[1] but in 2-chloropropenal a nonplanar second conformer with a C=C—C=O torsion angle of 135–145° was found. It is, however, difficult to know how far from planar this second form really is. A planar molecule with a large torsional vibration will appear nonplanar unless a dynamic model is used in the refinements. Such a dynamic model was not tried for 2-chloropropenal, and it is therefore possible that 2-bromopropenal and 2-chloropropenal may have fairly similar conformational properties. Electron diffraction is not a very good methode for distinguishing between planar and slightly nonplanar forms.

ED investigations at more than one temperature have made it possible to determine energy and entropy differences between conformers for several of the substituted propenals.[5-7] For 2-bromopropenal experimental problems made it impossible to get data at more than one temperature. $\Delta E°$ and $\Delta S°$ can therefore not be determined directly. The most important contribution to the entropy will come from the low torsional vibrations. Since we found the two rms torsional amplitudes to be almost equal, it is not unreasonable to assume that the conformational entropy difference must be small. If we assume $\Delta S°$ to be zero, we can use our ED results to determine the difference in energy between the two conformers. The result is $\Delta E° = E_s° - E_a° = 1.7 \pm 1.4$ kJ/mol. This is larger than the value observed in propenoyl chloride[5] ($\Delta E° = 1.0 \pm 1.5$ kJ/mol) but smaller than the values found in 2-chloropropenoyl chloride[6] (3.8 ± 4.4 kJ/mol), 2-chloropropenal[7] (5.9 ± 2.1 kJ/mol), or propenal[1] (7.1 ± 0.2 kJ/mol). The presence of a large bromine atom in the 2-position of propenal therefore seems to reduce the stability of the anti conformer much more than a chlorine atom in this position will do. Both the Br···O distance in the anti form of 2-bromopropenal and the Cl···O distance in 2-chloropropenal are only slightly shorter than the sum of the corresponding van der Waals radii (3.08 versus 3.35 Å and 2.99 versus 3.20 Å). This can therefore not explain why the two molecules have different $\Delta E°$ values.

Table III shows a summary of geometrical parameters for 2-bromopropenal and some related molecules. Propenal and 2-bromopropenal have similar geometry; all comparable parameters are equal within errors limits. For 2-chloropropenal[7] the bonds are observed to be shorter, but since this is found for all the bonds, it may indicate a small scale-factor error in one or both of the 2-halopropenal investigations. The carbon–bromine bond is shorter in 2-bromopropenal than in oxalyl bromide[4] (1.883 (8)

Table II. Correlation Matrix (×100) for Parameters of 2-Bromopropenal

parameter	σ_{LS}[a]	r_1	r_2	r_3	r_4	r_5	$\angle_6$	$\angle_7$	$\angle_8$	$\angle_9$	$\angle_{10}$	$\angle_{11}$	$\angle_{12}$	l_{13}	%
1 *r*(C—H)	0.007	100	28	9	−23	1	−11	−45	−17	22	16	−8	−10	−32	2
2 *r*(C=O)	0.002		100	53	18	−15	16	−15	16	21	−32	−24	15	18	1
3 *r*(C=C)	0.003			100	54	−36	33	−6	42	7	−57	43	21	32	6
4 *r*(C—C)	0.003				100	−32	42	11	38	12	−67	49	20	46	10
5 *r*(C—Br)	0.002					100	41	34	−37	−1	25	4	−2	−11	4
6 ∠C—C=C	0.37						100	45	−19	11	−27	47	13	30	19
7 ∠C=C—H	3.06							100	−27	−48	2	28	14	9	9
8 ∠C—C—Br	0.62								100	−2	−65	−11	37	30	−33
9 ∠C—C—H	3.22									100	8	2	−8	42	8
10 ∠C—C=O	0.56										100	−44	−23	−27	−6
11 σ_a[b]	3.30											100	−3	26	49
12 σ_S[b]	4.59												100	15	−56
13 *l*(C—Br)	0.003													100	13
14 % anti	3.66														100

[a] Standard deviations from least squares; distances and amplitudes in ångströms, angles in degrees. [b] Rms torsional amplitudes for anti and syn.

Table III. Geometrical Parameter Values for 2-Bromopropenal and Related Molecules

molecule	*r*(C=O)	*r*(C=C)	*r*(C—C)	(C—Br)	∠C—C=O	∠C—C=C	ref
propenal	1.217 (3)	1.345 (3)	1.484 (4)		123.3 (7)	120.3 (7)	2
2-chloropropenal	1.212 (3)	1.328 (6)	1.477 (6)		122.8 (15)	121.1 (6)	7
2-bromopropenal	1.219 (8)	1.350 (13)	1.498 (13)	1.883 (8)	124.0 (17)	121.7 (11)	this work
propenoyl chloride	1.192 (2)	1.339 (2)	1.484 (4)		125.2 (2)	123.4 (7)	5
2-chloropropenoyl chloride	1.188 (2)	1.341 (3)	1.495 (3)		125.5 (6)	122.0 (6)	6
oxalyl bromide	1.178 (2)		1.540 (5)	1.927 (3)	124.8 (3)		4

Å versus 1.927 (3) Å). This is in accordance with the earlier observed effect that bonds adjacent to carbonyl groups are longer than those adjacent to ethylene groups. The same effect is observed when comparing r(C–Cl) in 2-chloropropenal[7] (1.723 (2) Å) and in oxalyl chloride[3] (1.745 (2) Å), and also when comparing the two carbon–chlorine distances in 2-chloropropenoyl chloride[6] (1.731 (3) Å versus 1.773 (3) Å). A general shortening has been observed in r(C=O) when comparing the bond lengths of acid halides with those for aldehydes. Halogen substitution has not, however, been found to produce a similar shortening of a carbon–carbon double bond, and the results for 2-bromopropenal confirm this.

Using the harmonic approximation, values for the torsional force constants for the two conformers may be estimated from the rms torsional amplitudes ($k = RT/\sigma^2$). The obtained values are $k_{\text{anti}} = 0.027$ and $k_{\text{syn}} = 0.022$ mdyn·Å·rad^{-1} with standard deviations of 0.012 mdyn·Å·rad^{-1}. The torsional wavenumbers corresponding to these force constants are $\omega_{\text{anti}} = 84$ ($2\sigma = 38$) cm^{-1} and $\omega_{\text{syn}} = 70$ ($2\sigma = 39$) cm^{-1}. No spectroscopic observations of these vibrations have been made.

Acknowledgment. We are grateful to Anne Knapstad and Jostein Krane for preparing the sample and to Ragnhild Seip for help with the electron diffraction experiment. Financial support from the Norwegian Research Council for Science and the Humanities is acknowledged.

Registry No. 2-Bromopropenal, 14925-39-4.

Supplementary Material Available: Tables listing total intensities, final backgrounds, average molecular intensities, symmetry coordinates, and force constants (6 pages). Ordering information is given on any current masthead page.

Substituent Effects and Transition Structures for Diels–Alder Reactions of Butadiene and Cyclopentadiene with Cyanoalkenes

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Abstract: The transition structures for the reactions of butadiene with ethylene, acrylonitrile, maleonitrile, fumaronitrile, and 1,1-dicyanoethylene have been located with ab initio calculations using the 3-21G basis set. The transition structures for the reactions of cyclopentadiene with ethylene and acrylonitrile have also been located at the AM1 and 3-21G levels of theory. Relative activation energies with ab initio techniques follow the same trend as those obtained experimentally by Sauer et al. for the analogous reactions of cyclopentadiene and 9,10-dimethylanthracene with these dienophiles. Limited asynchronicity is obtained for the transition structures with unsymmetrical dienophiles.

The Diels–Alder reaction of butadiene with ethylene is a synchronous concerted reaction.[1-4] A C_s symmetrical transition structure is obtained by a variety of calculations. The calculations[5-10] that predict diradical intermediates appear to be in error. Unsymmetrical substitution will cause the transition structures of such reactions to become asynchronous, and it has been suggested that the mechanism will then involve diradical intermediates or at least biradicaloid transition structures.[5,9] We now present quantum mechanical calculations that address the role of unsymmetrical substitution upon the reaction mechanism.

The major points of interest of this study are as follows: (1) What is the degree of asynchronicity in the transition structures of the Diels–Alder reaction of butadiene and cyclopentadiene with unsymmetrically substituted cyanoethylenes? (2) Are the incorrect AM1 predictions of the trends in the activation energies for cyanoalkene Diels–Alder reactions an inherent failing of that method or do they support the biradical mechanism, as Dewar claims?[5] How do ab initio calculations perform? (3) Do Diels–Alder reactions of the more electron-rich cyclopentadiene give lower activation energies than the corresponding Diels–Alder reactions of butadiene in accordance with experimental observations,[11] and how do these transition structures vary?

Computational Method

Transition structures were obtained with Pople's GAUSSIAN 82 and 86 programs[12,13] via RHF calculations with the STO-3G and 3-21G basis sets.[14] All structures were optimized with analytical gradient methods. Single-point calculations with the 6-31G* basis set and MP2 correlation

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