

Chiroptical Properties of the Ketene and Diazo Chromophores. 1. Conformation and Optical Activity of 1-Alken-1-ones and 1-Diazoalkanes vs Aldehydes

Gennady V. Shustov, Fang Sun, Ted S. Sorensen, and Arvi Rauk*

Department of Chemistry, The University of Calgary, Calgary, Alberta T2N 1N4, Canada

Received August 29, 1997

Ab initio methods have been employed to study the conformational behavior and chiroptical properties of acyclic, structurally related aldehydes, ketenes, and diazoalkanes of the type MeCHRCH=XY. The study involved aldehydes **1**, **4**, and **7** (XY = O, R = H, Me, Et, correspondingly), ketenes (1-alken-1-ones) **2**, **5**, and **8** (XY = CO, R = H, Me, Et), and 1-diazoalkanes **3**, **6**, and **9** (XY = NN, R = H, Me, Et). Geometries were optimized at the B3LYP/6-31G* level, stationary points were characterized by vibrational frequency analysis, and final energies of **7–9** were obtained at the B3LYP/6-311+G**//B3LYP/6-31G* level. The chiroptical properties were calculated by the CIS/6-31+G* method. It was found that rotational barriers of the functional group (CHXY) about the CC bond are lowered in the following order: aldehydes (1.5–2.1 kcal mol⁻¹) > ketenes (1.3–1.6) > diazoalkanes (0.5–0.7). A conformer with the C=X bond eclipsed by an α -hydrogen is the global minimum of the ketenes and diazoalkanes, unlike the aldehydes where eclipsing by an α -alkyl group is preferred over a hydrogen. In all three classes of compounds, the optical rotational strength of the $n\text{-}\pi^*$ transition is greatest for conformers with the dihedral angle, CCCX, in the range 80–100°. Within this range, the signs of the $n\text{-}\pi^*$ rotational strengths for the ketenes and diazoalkanes are opposite to ones for the aldehydes. As a whole, the torsional dependencies of the $n\text{-}\pi^*$ rotational strength of the ketene and diazo chromophores can be explained within the framework of a model of “through-bond” perturbation. CD spectra of (*S*)- α -methyl-substituted butanal (**7**), 1-penten-1-one (**8**), and 1-diazobutane (**9**) were obtained experimentally. The calculated chiroptical properties of equilibrium mixtures of conformers of compounds **7–9** are in agreement with experimental data.

Introduction

From the point of view of the local molecular symmetry and of the $n\text{-}\pi^*$ orbital origin of the lowest electronic transition, the ketene¹ and diazo (diazoalkane)² groups are analogues of the carbonyl group, investigations of chiroptical and conformational properties of which are a cornerstone of modern stereochemistry.^{3,4} Nevertheless, this aspect of ketenes and diazoalkanes has not been studied so far. To the best of our knowledge, there is no published CD spectrum of a compound with an isolated ketene or diazo chromophore.⁵ The paucity of published data is pretty astonishing because the $n\text{-}\pi^*$ transitions of these chromophores are observed at longer wavelengths (320–380 and 450–510 nm,² respectively) than the corresponding transition of a carbonyl (290–300 nm),⁴ and therefore, the Cotton effects (CE) could be measured more readily.

It should be noted that, unlike the vast literature on the CD of ketones,⁴ there are few articles⁶ regarding the chiroptical properties of aldehydes. As follows from the reviews,⁴ almost all works on the CD of ketones are devoted to the study of relatively stereochemically rigid cyclic and bicyclic compounds, for which a connection between a CE sign and stereochemistry of a molecule can be easily established. On the other hand, analysis of conformationally mobile systems, to which the aldehydes belong, is quite complex. For the correct correlation of the sign of a CE with the stereochemistry of the chromophore environment in such a system, an estimation of the contribution of each stable conformer in the observed CE is necessary. The *ab initio* calculations employed in the present work provide a solution for this problem.

We have carried out theoretical studies of the conformationally mobile aldehydes **1**, **4**, and **7**, ketenes **2**, **5**, and **8**, and diazoalkanes **3**, **6**, and **9** by means of *ab initio* calculations of their ground and excited states. Compounds **7–9** had been synthesized and their experimental CD spectra were compared with the calculated data. The main objectives of the calculations of the simple model compounds **1–6** were to compare conformational properties of compounds bearing ketene and diazo groups with the carbonyl compounds and to obtain a mapping of the perturbing influence of α -alkyl substituents on the optical activity connected with the $n\text{-}\pi^*$ transitions of the

* To whom correspondence should be addressed. Phone: (403) 220-6247. Fax: (403) 289-9488. E-mail: rauk@chem.ucalgary.ca.

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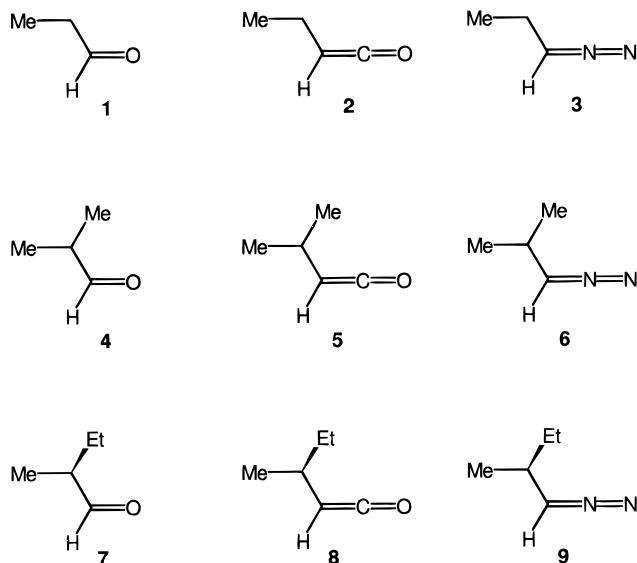
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structurally related chromophores. This information would then lay the foundation for understanding of the chiroptical properties of all three classes of chromophores, as exemplified by compounds 7–9.

The flow of the paper is as follows. After a description of the theoretical and experimental procedures, we discuss the calculated potentials for internal rotation of the aldehyde, ketene, and diazo groups in compounds 1–6. The factors, which influence the rotational barriers and relative stability of the conformers, differ among the three classes of compounds, and these differences are rationalized using concepts from simple orbital interaction theory. The preliminary choice of the stable conformers of the more complex molecules 7–9 was made on the basis of these data. Second, we determine the nature of the lowest electronic state of each chromophore and observe that the nodal properties of the orbitals involved in the first electronic transition imply the possibility of application of an octant rule to the ketene and diazo chromophore as well as the carbonyl. We find that the calculated torsion angular dependencies of the “ $n-\pi^*$ ” rotational strengths for models 1–6 are consistent with a “through-bond” mechanism for the perturbation by the substituent. Last, using the model findings and the calculated and experimental signs of the $n-\pi^*$ CEs of equilibrium mixtures of their stable conformers, we analyze the chiroptical properties of compounds 7–9.

Computational Methods

Geometries of the stationary structures of compounds 1–9 were fully optimized at the Becke3LYP theoretical level with the internal 6-31G* basis set, using procedures implemented in the Gaussian 92^{7a} and Gaussian 94^{7b} systems of programs. Harmonic frequency analysis verified the nature of the stationary points as minima (all real frequencies) or as transition structures (one imaginary frequency) and was used to provide an estimate of the zero-point vibrational energies (ZPVE).

Selected calculated geometrical parameters, dipole moments, and relative energies of the stationary structures of compounds 1–3 and 4–6 are given in Tables S-1 and S-2 of the Supporting Information, correspondingly.

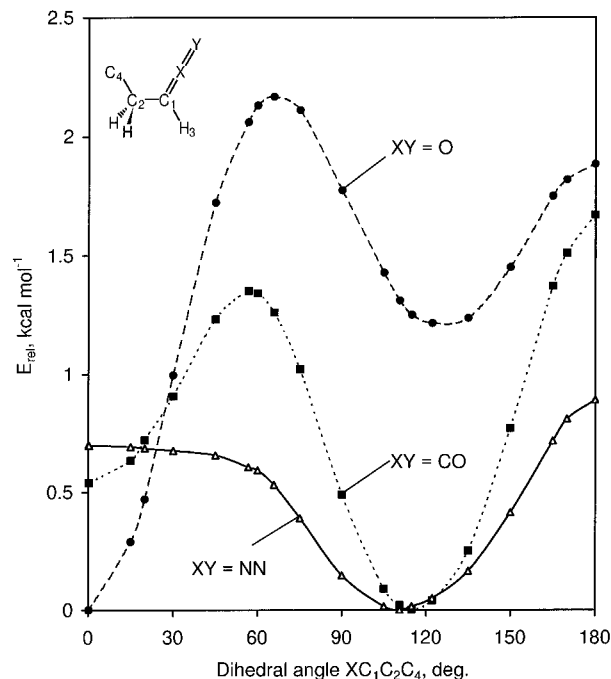


Figure 1. Rotational potential energy curves for α -monomethyl compounds 1–3 derived with B3LYP/6-31G*.

Intermediate points of the rotational potentials (Figures 1 and 2) were calculated by freezing of the $XC_1C_2C_4$ dihedral angle and optimization of all other geometrical parameters.

Final energies of 7–9 were obtained at the B3LYP/6-311+G**//B3LYP/6-31G* level. Heat capacities and entropy corrections were made using scaled frequencies and standard statistical procedures based on the rigid rotor-harmonic oscillator model⁸ to determine enthalpies and free energies for stable conformers of 7–9. Zero-point corrections ($\Delta ZPVE$) and the frequencies were scaled by a factor of 0.95. All normal modes were treated as vibrations except for the lowest, which had a frequency of less than 50 cm^{-1} and corresponded in each case to a rotation about the C–C bond to the trigonal carbon atom. For the purpose of calculating heat capacities and entropies, this mode was removed from the list of vibrations and treated as a free rigid rotor. Table S-3 of the Supporting Information shows relative energies, $\Delta ZPVE$, and thermodynamic parameters (ΔS^0 , ΔH^0) of the conformers of 7–9.

For all chiral species, chiroptical properties were calculated by single point all-singles configuration interaction (CIS) calculations⁷ with the 6-31+G* basis set at the Becke3LYP geometries. The use of diffuse s and p

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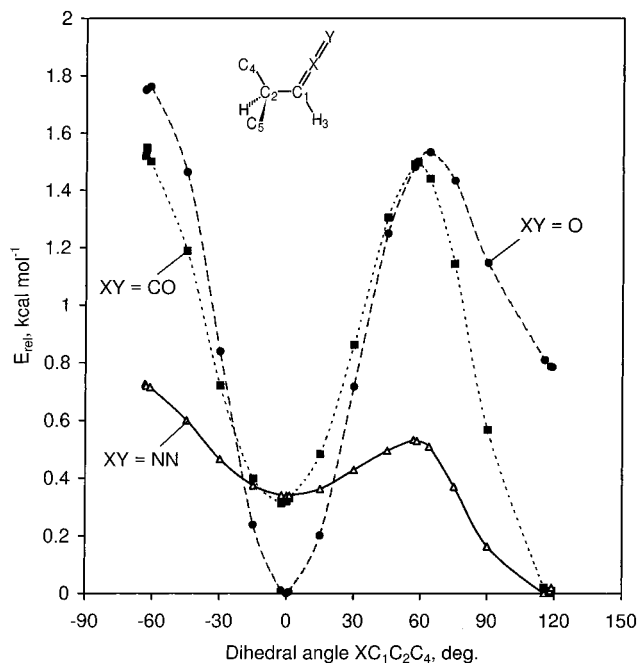


Figure 2. Rotational potential energy curves for α,α -dimethyl compounds **4–6** derived with B3LYP/6-31G*.

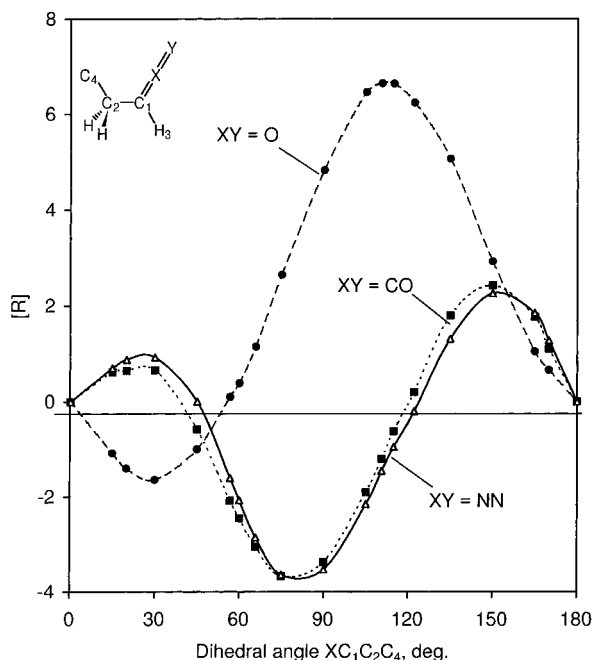


Figure 3. Torsional $n-\pi^*$ optical rotational strength dependencies for α -monomethyl compounds **1–3** derived with CIS/6-31+G**/B3LYP/6-31G*.

functions designated by the “+” is desired for a more accurate description of the excited singlet states. The CIS calculation is carried out for a specific number of electronic states, and values of electric and magnetic dipole transition moments are calculated. The magnetic dipole transition moments as produced by the Gaussian programs are for a ground- to excited-state transition and must be reversed in sign when used to calculate optical rotational strengths. The calculated torsional dependencies of rotational strengths of the $n-\pi^*$ transitions in compounds **1–3** and **4–6** are shown in Figures 3 and 4, respectively. Tables **1–3** show calculated chiroptical properties of the conformers of **7–9** along with dihedral

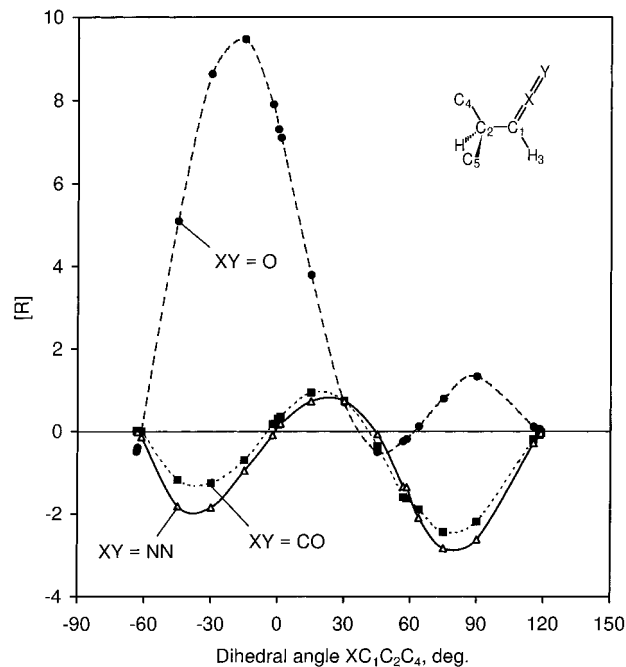


Figure 4. Torsional $n-\pi^*$ optical rotational strength dependencies for α,α -dimethyl compounds **4–6** derived with CIS/6-31+G**/B3LYP/6-31G*.

angles, free energy changes (ΔG^0), and populations of these conformers.

Molecular orbitals of **1–3** (Figure 5) are displayed as modified Jorgensen–Salem plots.⁹

Experimental Section

(S)-(+)-2-Methylbutanal (7) $[[\alpha]^{20}_D: +34.3$ (c 2.5, acetone); CD in n -heptane at 20° , λ_{max} , nm ($\Delta\epsilon$) 311 (0.065); Figure 6] was prepared from **(S)-(-)-2-methyl-1-butanol** $[[\alpha]^{23}_D -5.8$ (neat), Aldrich] according to the procedure of Anelli et al.¹⁰

(S)-3-Methyl-1-penten-1-one (8). The **(S)-2-bromo-3-methylpentanoic acid** was made from **L-(2S,3S)-isoleucine**¹¹ and its acid chloride prepared using SOCl_2 . A solution of the acid chloride (10 mg, 0.047 mmol) in methylene chloride (0.5 mL) was added by syringe to a solution of $\text{PPN}^+\text{Cr}(\text{CO})_4\text{NO}^-$ (60 mg, 0.082 mmol)¹² in methylene chloride (1 mL), with stirring at -78°C under nitrogen. After 10 min, pentane (6 mL) was slowly added. Stirring was continued for 10 min and the mixture allowed to stand for 1 h at -78°C . The clear supernatant solution was used for the CD determination (Figure 6) λ_{max} , nm ($\Delta\epsilon$) 363 (0.041), assuming a theoretical concentration of 4.6 mg/7.5 mL 4:1 pentane/methylene chloride. The measurement was made at -13°C . The ketene formation had been verified in a preliminary experiment using deuteriomethylene chloride solvent, and NMR spectroscopy was used as a structure assignment tool for this in situ preparation. ^1H NMR at -70°C (J , Hz): δ 0.81 (t, 3H, $^3J = 7.3$); 0.98 (d, 3H, $^3J = 6.7$); 1.05–1.20 and 1.30–1.40 (1H each, both m); 2.13 (m, 1H) and 2.75 (1H, d, $^3J = 6.9$). ^{13}C : δ 11.4 (CH_3); 21.4 (CH_3); 22.9 (CH); 28.2 (CH); 31.3 (CH_2) and 200.2 ($\text{C}=\text{O}$).

(S)-(+)-2-Methyl-1-diazobutane (9). A modification of the procedure of Kaufman et al.¹³ was used. A solution of **(S)-(+)-**

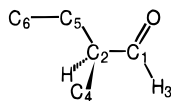
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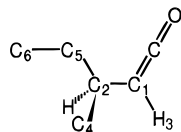
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Table 1. Calculated Parameters^a for the First ($n\text{-}\pi^*$) Electronic Transition of the Conformers of (*S*)-2-Methylbutanal (7**) along with Dihedral Angles,^b Free Energy Changes,^c and Populations^d of These Conformers**

	<i>ss-7a</i>	<i>ss-7b</i>	<i>ss-7c</i>	<i>sc-7a</i>	<i>sc-7b</i>	<i>sc-7c</i>	<i>cs-7a</i>	<i>cs-7b</i>	<i>cs-7c</i>
$D(\text{OC}_1\text{C}_2\text{C}_4)$	115.9	123.5	148.6	-5.0	-0.4	0.3	-116.9	-128.2	-138.2
$D(\text{OC}_1\text{C}_2\text{C}_5)$	-121.7	-112.8	-85.3	120.4	126.7	128.2	8.4	-0.9	-8.4
$D(\text{C}_1\text{C}_2\text{C}_5\text{C}_6)$	65.5	175.5	-63.9	65.8	167.6	-67.1	69.3	169.3	-70.5
ΔE	4.93	4.93	4.85	4.92	4.97	4.97	4.96	4.97	4.95
λ	252	252	256	252	249	249	250	249	251
[R]	+1.4	-2.2	+0.5	+6.5	+9.2	+6.9	-10.1	-6.8	-4.6
f	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001	0.0002	0.0002	0.0001
ΔG_{293}^0	0.00	0.60	2.12	1.03	0.12	0.65	0.38	0.36	1.46
p (at 20 °C)	26.2	9.3	0.7	4.4	21.1	8.5	13.6	14.1	2.1

^a CIS/6-31+G**/B3LYP/6-31G*; the transition energies (ΔE) are given in eV, the wavelengths (λ) in nm, the rotational strengths ([R]) in $\text{cgs} \times 10^{-40}$, the oscillator strengths (f) in cgs . ^b B3LYP/6-31G* optimized geometries; the dihedral angles (D) in degrees. ^c The free energies (ΔG^0) in kcal mol^{-1} derived with B3LYP/6-311+G**/B3LYP/6-31G*; see Table S-3 for other thermodynamic parameters. ^d The populations (p) in %.

Table 2. Calculated Parameters^a for the First ($n\text{-}\pi^*$) Electronic Transition of the Conformers of (*S*)-3-Methyl-1-penten-1-one (8**) along with Dihedral Angles,^b Free Energy Changes,^c and Populations^d of These Conformers**

	<i>ss-8a</i>	<i>ss-8b</i>	<i>ss-8c</i>	<i>sc-8a</i>	<i>sc-8b</i>	<i>sc-8c</i>	<i>cs-8a</i>	<i>cs-8b</i>	<i>cs-8c</i>
$D(\text{CC}_1\text{C}_2\text{C}_4)$	118.8	110.1	117.2	-8.3	-4.0	-3.2	-110.9	-121.0	-137.3
$D(\text{CC}_1\text{C}_2\text{C}_5)$	-117.3	-116.7	-116.4	116.8	121.9	124.1	14.5	5.0	-9.9
$D(\text{C}_1\text{C}_2\text{C}_5\text{C}_6)$	63.9	174.7	-61.8	59.7	169.7	-65.0	66.2	172.5	-67.5
δE	4.01	4.00	4.04	4.01	3.97	3.98	3.96	3.97	3.96
λ	309	310	307	309	312	312	313	312	313
[R]	+1.4	-0.3	-0.3	-0.4	+1.4	-0.4	+0.3	-0.5	-0.6
f	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ΔG_{260}^0	0.00	0.5	1.3	0.7	1.0	1.5	1.3	1.1	2.2
p (at -13 °C)	47.6	18.1	3.6	11.4	6.7	2.5	3.7	5.8	0.6

^{a-d} See the corresponding footnotes to Table 1.

2-methylbutanal (0.517 g, 6 mmol) in absolute ether (5 mL) was added to a stirred mixture of tosylhydrazine (0.931 g, 5 mmol), molecular sieves (4 Å, 3.5 g), and absolute ether (30 mL). The stirring was continued at rt for 0.5 h, and the reaction mixture was filtered and evaporated in vacuo. The residue was recrystallized from a mixture of *n*-hexane-ether at -30 °C to provide (*S*)-2-methylbutanal tosylhydrazone (1.132 g, 89%), mp 66–67 °C. ¹H NMR in CDCl₃ (J , Hz): δ 0.75 (t, 3H, ³ J = 7.3), 0.98 (d, 3H, ³ J = 7.0), 1.32 and 1.41 (1H each, both m, ² J = 14.7, ³ J = 7.3, 6.7), 2.22 (m, 1H, ³ J = 7.0, 6.7, 6.1), 2.43 (3H), 7.05 (d, 1H, ³ J = 6.1), 7.28 and 7.80 (dd, 4H, ³ J = 8.5).

A solution of (*S*)-2-methylbutanal tosylhydrazone (1.017 g, 4 mmol) in absolute ether (20 mL) was added to a stirred suspension of NaH (0.115 g, 4.8 mmol) in absolute ether (5 mL). The reaction mixture was stirred at rt for 2 h, and the solvent was removed in vacuo. The dry sodium salt was heated on an oil bath to 140–150 °C under a vacuum of 0.25 mm. Diazoalkane **9** as an orange liquid (0.330 g, 84%) was collected in a trap cooled by a dry ice-acetone bath, $[\alpha]_{\text{D}}^{15} +54.3$ (c 4.1, *n*-heptane). ¹H NMR in C₆D₆ (J , Hz): δ 0.70 (t, 3H, ³ J = 7.3), 0.77 (d, 3H, ³ J = 6.7), 1.06 (m, 2H, ² J = 13.4, ³ J = 7.3, 6.1), 1.83 (m, 1H), 2.87 (d, 1H, ³ J = 5.2). CD in *n*-heptane at 20 °C, λ_{max} , nm ($\Delta\epsilon$): 489 (0.032), 465 (0.030), 240 (-0.145), 223 (1.27). UV in *n*-heptane, λ_{max} , nm (ϵ): 467 (8), 229 (16 200); Figure 7.

Results and Discussion

Conformation. Geometries, dipole moments, and relative energies of conformers of propanal (**1**)¹⁴ and 2-methylpropanal (**4**)¹⁵ were previously measured experimentally by means of IR and microwave spectroscopy. As one can see from Tables S-1 and S-2 (Supporting Information), the experimental data are well reproduced by the calculations at the Becke3LYP/6-31G* level of theory. The obtained potentials for internal rotation of the aldehyde group in **1** and **4** (Figures 1 and 2) are similar to those calculated by Wiberg¹⁶ at the MP3/6-31G**/RHF/3-21G (for **1**) and RHF/6-31G**/RHF/3-21G (for **4**) levels. Wiberg¹⁶ suggested that the relative

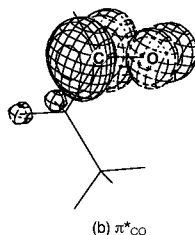
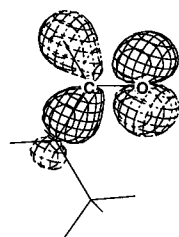
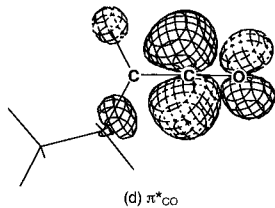
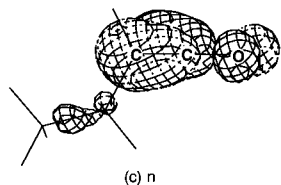
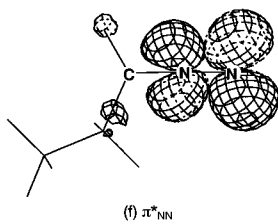
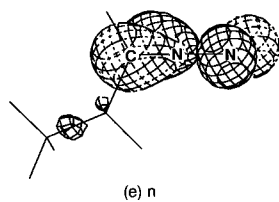
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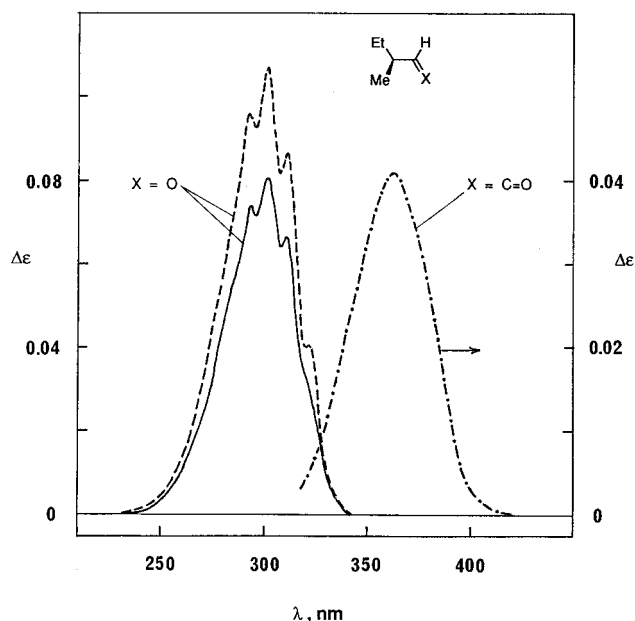
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Table 3. Calculated Parameters^a for Three Electronic Transitions of the Conformers of (*S*)-2-Methyl-1-diazobutane (**9**) along with Dihedral Angles,^b Free Energy Changes,^c and Populations^d of These Conformers

	<i>ss</i> - 9a	<i>ss</i> - 9b	<i>ss</i> - 9c	<i>sc</i> - 9a	<i>sc</i> - 9b	<i>sc</i> - 9c	<i>cs</i> - 9a	<i>cs</i> - 9b	<i>sc</i> - 9c
$D(\text{NC}_1\text{C}_2\text{C}_4)$	114.6	122.8	135.3	-31.7	-3.8	-3.6	-100.0	-124.8	-160.1
$D(\text{NC}_1\text{C}_2\text{C}_5)$	-121.3	-112.6	-98.2	94.4	122.3	123.8	26.0	1.3	-33.9
$D(\text{C}_1\text{C}_2\text{C}_5\text{C}_6)$	63.4	174.3	-60.9	58.2	168.8	-65.3	63.3	172.5	-63.3
$S_0 \rightarrow S_1$ ($n-\pi^*_{\text{NN}}$)									
ΔE	2.81	2.80	2.82	2.80	2.77	2.77	2.77	2.76	2.78
λ	442	443	440	443	448	448	448	449	446
[R]	-0.08	+0.6	+1.7	-1.7	+0.8	+0.04	+2.4	-0.5	-1.2
f	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$S_0 \rightarrow S_2$ ($n-3s$)									
ΔE	5.87	5.82	5.82	5.83	5.81	5.82	5.87	5.82	5.83
λ	211	213	213	213	213	213	211	213	213
[R]	-1.2	-0.6	1.2	+2.2	-1.9	-2.4	-0.7	+2.4	+11.5
f	0.0065	0.0071	0.0073	0.0128	0.0077	0.0063	0.0065	0.0072	0.0042
$S_0 \rightarrow S_3$ ($n-3p$)									
ΔE	6.36	6.31	6.32	6.26	6.26	6.32	6.27	6.25	6.27
λ	195	196	196	198	198	196	198	198	198
[R]	+2.4	-3.3	-12.6	+15.8	+15.7	+9.1	+8.9	-13.2	+3.4
f	0.3321	0.3310	0.3316	0.2893	0.2774	0.2863	0.2814	0.3046	
ΔG°_{293}	0.00	0.5	1.3	0.9	1.2	1.6	1.0	1.4	
p (at 20 °C)	45.9	18.1	5.1	9.4	6.0	2.9	8.2	4.3	

^{a-d} See the corresponding footnotes to Table 1.Aldehyde *c*-1Ketene *s*-2Diazoalkane *s*-3**Figure 5.** The n and π^* orbitals involved in the first electronic transition of aldehyde **1** (a, b), ketene **2** (c, d), and diazoalkane **3** (e, f).

energies of the conformers of aldehydes **1** and **4** are determined by, mainly, the CO dipole-CC-induced dipole (DID) interaction, which stabilizes *cis*-conformers *c*-1

**Figure 6.** CD spectra of (*S*)-2-methylbutanal (**7**) in heptane at 20 °C (—) and -13 °C (---) and of (*S*)-3-methyl-1-penten-1-one (**8**) in a mixture of pentane- CH_2Cl_2 (4:1 v/v) at -13 °C.

and *cs*-**4** with eclipsed carbonyl and methyl groups (Chart 1).

We suppose that two more factors due to orbital interactions have to be taken into account. First, there is a balance of the steric interactions (the aggregate of four-electron two-orbital interactions) arising from the eclipsing of the hydrogen or oxygen atom of the aldehyde group by an α -substituent (α -hydrogen or methyl group). Since the valence angle $\text{C}_2\text{C}_1\text{H}_3$ is nearly 10° smaller than the angle OC_1C_2 (Chart 2; Tables S-1 and S-2, Supporting Information), the steric destabilization of conformers *g*-**1**, *t*-**1** and *gg*-**4**, *tg*-**4** with the eclipsed aldehyde hydro-

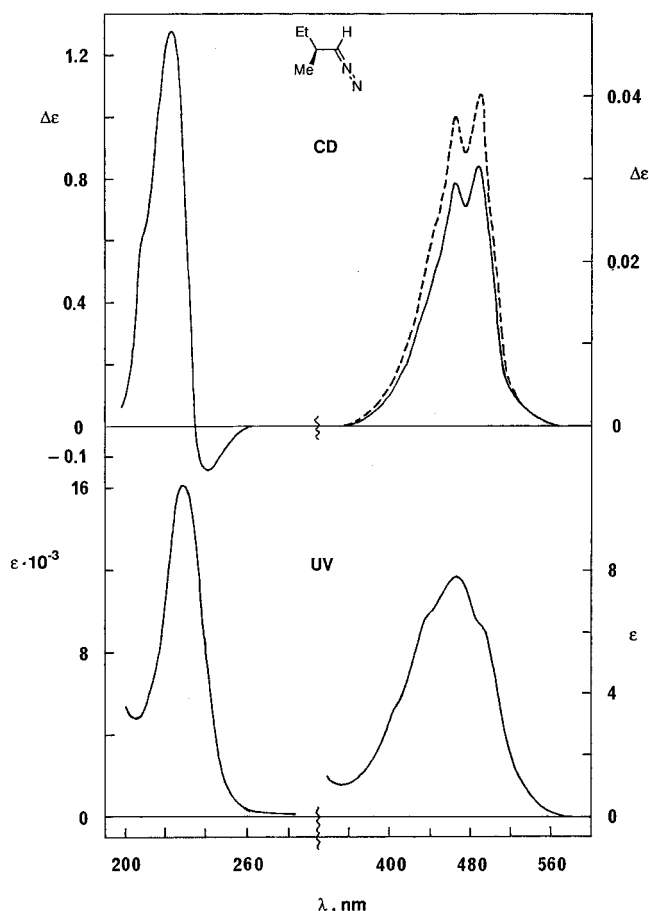


Figure 7. CD and UV spectra of (*S*)-2-methyl-1-diazobutane (**9**) in heptane at 20 °C (—) and -13 °C (---).

gen atom is greater than conformers *c-1*, *s-1* and *cs-4*, *ss-4* with the eclipsed oxygen. Thus, for aldehydes, these steric repulsions work in the same direction as the DID interaction.

The attractive two-electron two-orbital interaction¹⁷ of the methylene π orbital in **1** or the methyne σ orbital in **4** with the antibonding π^*_{CO} orbital is the second factor. In parallel with the DID interaction and the minimum steric repulsions, the $\pi_{CH_2}(\sigma_{CH})-\pi^*_{CO}$ interaction stabilizes rotamers *c-1* and *cs-4*, making them the global minima. In the cases of *t-1* and *tg-4*, this interaction cannot compensate the steric H_3-Me repulsion and the destabilizing DID interaction, although it decreases the energies of these rotational transition states in comparison with the energies of other transition states, *g-1* and *gg-4*, with unfavorable orientation of the $\pi_{CH_2}(\sigma_{CH})$ and π^*_{CO} orbitals.

Narrowing of the valence angles XC_1H_3 and XC_1C_2 and, correspondingly, the expansion of the angle $C_2C_1H_3$ are observed in the sequence from aldehydes **1**, **4** to ketenes **2**, **5** and further to diazoalkanes **3**, **6** (Chart 2; Tables S-1 and S-2, Supporting Information). One can attribute this change in C_1 valence angles to the interaction of the occupied π like orbital of the fragment $C_2C_1H_3$ (π_{CCH} , the out-of-phase combination of the occupied σ orbitals of the C_2C_1 and C_1H_3 bonds) with orbitals of the XY group (Chart 2). In the aldehydes, the repulsion of the π_{CCH} orbital with the nonbonding n_O orbital of the oxygen

Chart 1

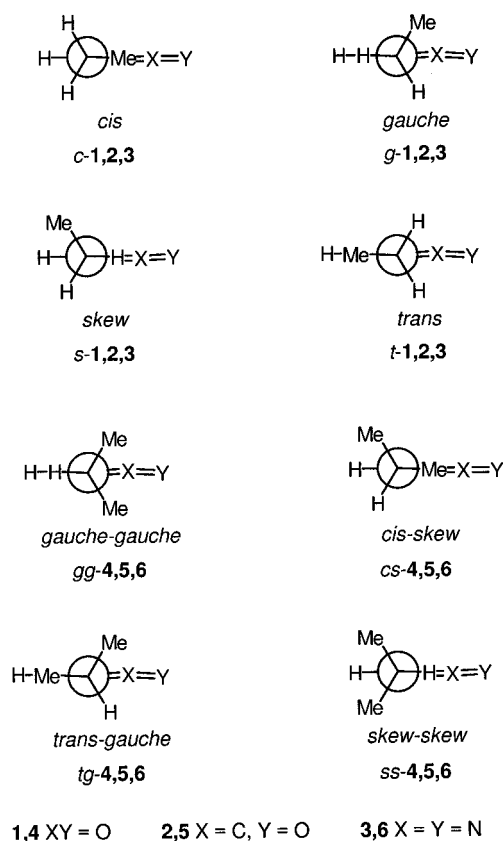
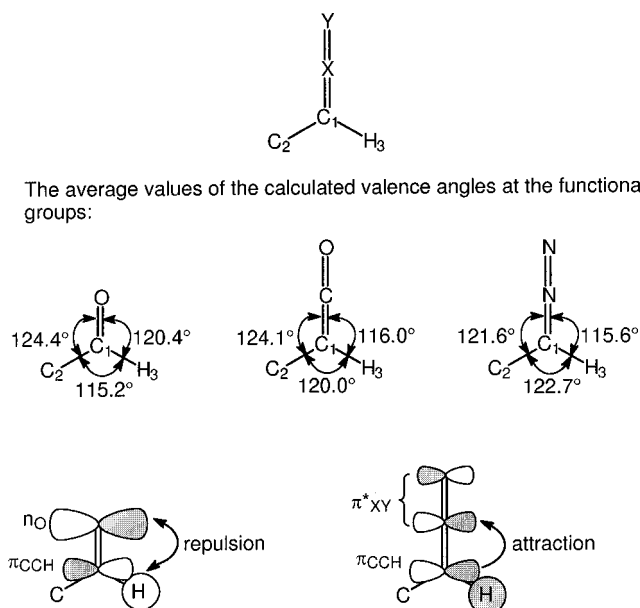


Chart 2

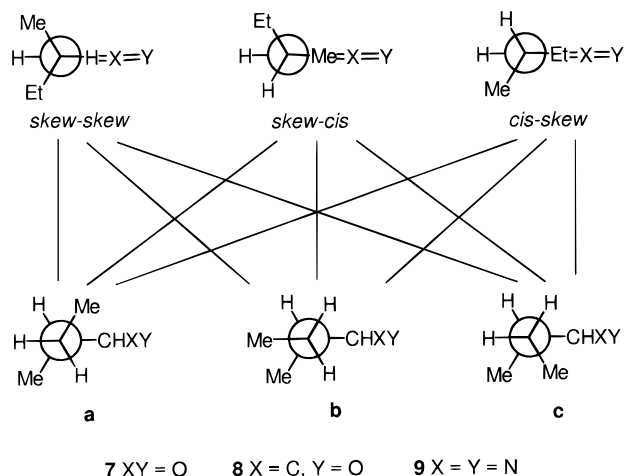


atom leads to the expansion of the valence angles OC_1H_3 and OC_1C_2 . In the ketenes and diazoalkanes, a possibility of the attractive interaction of the π_{CCH} orbital with the antibonding π^* orbitals of the CO and NN bonds, respectively, appears. Owing to this attractive interaction not present in aldehydes, the valence angles XC_1H_3 and XC_1C_2 in ketenes and diazoalkanes are reduced.

The presence of the above-mentioned orbital interactions is confirmed by the calculations. As one can see from Figure 5, the HOMO of the aldehyde **1** is the out-of-phase combination of the n_O and π_{CCH} orbitals. An

(17) Pross, A.; Radom, L.; Riggs, N. V. *J. Am. Chem. Soc.* **1980**, *102*, 2253–2259.

Chart 3



admixture of the π_{CCH} orbital to the antibonding π^*_{CO} and π^*_{NN} orbitals in the LUMO's of ketene **2** and diazoalkane **3**, respectively, is also noticeable.

The increase of the valence angle $\text{C}_2\text{C}_1\text{H}_3$ in the ketene group leads to a decrease of the steric repulsions of H_3 with the eclipsed α -substituent in conformers *g*-**2**, *t*-**2** and *gg*-**5**, *tg*-**5**. The small narrowing of the angle XC_1C_2 has to yield some strain in rotamers *c*-**2**, *s*-**2**, and *cs*-**5**, *ss*-**5**. It explains the lowering of the rotational barriers about the C_1C_2 bond in ketenes **2** and **5** in comparison with aldehydes **1** and **4** (Figures 1 and 2; Tables S-1 and S-2, Supporting Information). Besides, the ketene $\text{C}_1=\text{C}$ bond is a poorer acceptor than the aldehyde $\text{C}_1=\text{O}$ bond because the π^* orbital lies higher on energy and is polarized in the opposite direction, i.e., away from the C_1 atom. Therefore, in ketenes **2** and **5**, the stabilizing $\pi_{\text{CH}_2}(\sigma_{\text{CH}}) - \pi^*_{\text{CX}}$ interaction will be smaller and the destabilizing $\pi_{\text{CH}_2}(\sigma_{\text{CH}}) - \pi_{\text{CX}}$ one greater than in aldehydes **1** and **4**. As a result, conformers *s*-**2** and *ss*-**5** become more stable than conformers *c*-**2** and *cs*-**5**, respectively. For the same reasons, destabilization of transition state *t*-**2** relative to *g*-**2** and equalization of the energies of transition states *tg*-**5** and *gg*-**5** are observed.

The further expansion of the valence angle $\text{C}_2\text{C}_1\text{H}_3$ and the narrowing of the angle XC_1C_2 in diazoalkanes **3** and **6** led to the further lowering of the rotational barriers (Figures 1 and 2; Tables S-1 and S-2, Supporting Information). Moreover, the rotational potential of **3** becomes single-minimum, since the gauche-conformation is no longer a stationary point and lies rather lower than cis-rotamer *c*-**3**, that in its turn is now a saddle point. The rotational potential of diazoalkane **6** preserves the two-minimum shape, but it is appreciably more shallow than the potentials of aldehyde **4** and ketene **5**.

As follows from analysis of the rotational potentials of **4**–**6**, optically active aldehyde **7**, ketene **8**, and diazoalkane **9** are expected to exist in the form of stable *skew-skew*-, *skew-cis*-, and *cis-skew*-conformers, and each conformer in turn is represented by three isomers of the rotation around the CC bond to the ethyl group, i.e., **a**, **b**, **c** (Chart 3).

The calculations confirm the existence of these conformers as minima on the corresponding potential energy surfaces (Tables 1–3; Table S-3, Supporting Information). The only exception is the diazoalkane isomer *cs*-**9c** that was found as a saddle point. This isomer has the greatest relative energy ($1.6 \text{ kcal mol}^{-1}$; Table S-3, Supporting

Information) owing to steric strain, which is caused by the eclipsing of the ethyl and diazo groups and by the unfavorable arrangement of the terminal methyl group between the α -methyl and CHN_2 groups. The same isomer of ketene **8**, i.e., *cs*-**8c**, remains as a local minimum, but it also has the greatest relative energy (Table 2). In general, one observes for ketene **8** and diazoalkane **9** the following orders of increasing the conformers energies: $ss < sc < cs$ and $\mathbf{a} < \mathbf{b} < \mathbf{c}$. The narrowing of the valence angle $\text{C}_2\text{C}_1\text{H}_3$ and the increase of angle XC_1C_2 in aldehyde **7** led to an exception to this rule. The structures *ss*-**7a** and *sc*-**7b** were found as the predominant isomers that have almost identical energies on the vibrationless Born–Oppenheimer surface (Table S-3, Supporting Information). The zero-point correction makes *ss*-**7a** slightly more stable ($0.07 \text{ kcal mol}^{-1}$) than *sc*-**7b**. Unlike ketene **8** and diazoalkane **9**, *ss*-**7c** was found as the least stable isomer.

On the basis of the similarity of structures, compounds **7**–**9** are expected to have rotational barriers of the functional groups close to the barriers calculated for **4**–**6**, i.e., ca. $1.8 \text{ kcal mol}^{-1}$ for aldehyde **7**, ca. $1.5 \text{ kcal mol}^{-1}$ for ketene **8**, and ca. $0.7 \text{ kcal mol}^{-1}$ for diazoalkane **9**. It means virtually free rotation of the functional groups. In such a situation, the rigorous evaluation of the optical rotational strength of an equilibrium mixture of conformers would require the determination of the torsional angular dependencies of the energy and the optical rotational strength followed by numerical integration of these functions. Such a detailed procedure is beyond the scope of the present study. Rather, we calculate the conformationally averaged optical rotational strengths of compounds **7**–**9** by summing over the rotational strengths of the individual stable conformers weighted by the Boltzmann predicted equilibrium populations.

Optical activity. For aldehyde **7** and ketene **8**, only the first (long-wavelength) CE's were measured (Figure 6). In the case of ketene **8**, the accessible wavelength range is limited by the use of the solvent mixture (methylene chloride–pentane), which absorbs light at the region $< 310 \text{ nm}$. The CD spectrum of diazoalkane **9**, measured in the region 200 – 600 nm , contains at least three CE's (Figure 7). Ketene **8** is unstable at room temperature; therefore, its CD spectrum was recorded at $-13 \text{ }^\circ\text{C}$. For comparison, the first CE's of compounds **7** and **9** were also recorded at the same temperature.

The CIS calculations confirm the conventionally designated $n\text{-}\pi^*$ origin of the first electronic transition in aldehydes **1**, **4**, and **7**. The same designation is appropriate for the first transition in ketenes **2**, **5**, and **8** and diazoalkanes **3**, **6**, and **9** if one assigns the label "n" to the HOMO which is the out-of-phase combination of the $\pi_{\text{C}=\text{X}}$ orbital and a nonbonded orbital of the terminal O or N (Figure 5c,e). It is immediately apparent from Figure 5a that the "n₀" orbital of a carbonyl is also an out-of-phase combination of the nonbonding oxygen orbital with a π -like combination of the adjacent σ -bonds.

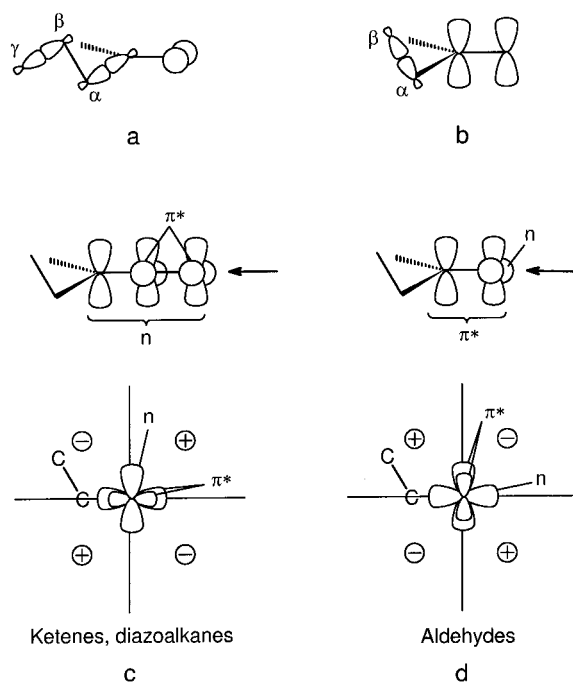
The subsequent two transitions in the diazo chromophore can be assigned to the n-3s and n-3p Rydberg transitions. The CIS method rather exaggerates the absolute values of transition energies, but the relative energies and order of the electronic transitions should be well reproduced. The calculated difference in the wavelengths ($\Delta\lambda = 244 \text{ nm}$) of the first and third transitions of diazoalkane **9** is close to the experimental one ($\Delta\lambda = 238 \text{ nm}$) measured from the UV spectrum of

this compound as the difference of the λ_{\max} values of the absorption bands at 467 and 229 nm (Figure 7). The second transition, weakly electric dipole allowed, is not observed in the UV spectrum of **9** in the background of the intense band of the n-3p transition at 229 nm.

The similarity of the molecular frameworks and the nodal structures of the frontier n and π^* orbitals of the ketenes/diazoalkanes and the carbonyl compounds supposes the possibility of division of space surrounding the ketene/diazo chromophore into octants⁴ that can be used for prediction of the sign of the rotational strength of the lowest (n- π^*) transition. However, the nodal planes of these ketene/diazo orbitals are orthogonal to the planes of the carbonyl orbitals. Also, in contrast to the n_0 orbital of the carbonyl chromophore, the initial n orbital of the ketene/diazo chromophore is mainly localized on the C₁ atom and the terminal π^* orbital on the terminal fragment XY (Figure 5). Therefore, one could expect the opposite sign of the induced rotational strength of the n- π^* transition in the ketene/diazo chromophore in comparison with the carbonyl chromophore for the same spatial arrangement of a perturber, i.e., anti-octant behavior. Indeed, as one can see from the torsional dependencies of rotational strengths of the n- π^* transitions calculated for the simplest compounds **1–3** (Figures 3 and 4), the rotational strength signs for the ketene/diazo chromophore are opposite to the ones for the carbonyl chromophore in the region of the dihedral angle $XC_1C_2C_4$ from 0 to 120°. In all cases, the maximum values of [R] are attained at the dihedral angle about 80–100°, i.e., at the greater overlapping of the π system of the functional group and the perturbing C₂C₄ bond. The decrease of the overlap as the dihedral angle decreases from 50 to 0° leads to a change of the sign of the rotational strength and to a decrease of its absolute value. Such a behavior is, in principle, in accord with a model of “through-bond” interaction offered by Kirk and Klyne^{4b,18a} and developed by Lightner and Bouman.^{4c,18b–d} In the first instance, the perturbing influence of a substituent at the β -carbon atom on the rotational strength of the carbonyl n- π^* transition was considered within the framework of this model. The perturbation acts through the interaction of the σ orbital of the C _{β} C _{γ} bond with the lone pair of the oxygen atom (Chart 4a), whereas the σ orbital of the C _{α} C _{β} (C₂C₄) bond in compounds **1–3** interacts mainly with the π orbital of the C₁X bond if the dihedral angle $XC_1C_2C_4$ is in the range of 80–100° (Chart 4b).

As has been previously shown,^{4b,18a} the maximum overlapping (a zigzag path for the β -substituent and n_0 orbital) of the interacting orbitals leads to a consignate contribution of the perturber in the n- π^* CE, and a decrease of the overlapping can yield a dissignate contribution. Examination of the torsional dependencies of the n- π^* rotational strengths of ketene **2** and diazoalkane **3** within the framework of the “through-bond” interaction model enables one to assume the sign distribution of the back octants shown in Chart 4c. It appears that the model in application to the α -methyl perturber works

Chart 4



better in the case of the ketene/diazo chromophore in comparison with the carbonyl one because the n- π^* rotational strengths of ketene **2** and diazoalkane **3** change their signs with a decrease of the σ - π overlapping not only in the 0–45° region but also in the 120–180° one, whereas the rotational strength sign of aldehyde **1** remains the same in the latter region as in the region of the maximum σ - π interaction.

One can suppose that the alteration of the rotational strength signs of the ketene/diazo chromophore is caused, as in the case of the carbonyl chromophore,^{4c,18d} by alteration of the mechanism of origin of optical activity. On the other hand, a conception of third surface^{4c,18b–e} might be used for explanation of dissignate contributions of substituents in the n- π^* CE of the ketene/diazo chromophore. However, further accumulation of experimental data and additional theoretical studies are necessary to locate this surface. In the present paper, we will be confined to examination of the back octants.

The sign distribution predicted for the back octants of the ketene and diazo chromophores is the same as deduced for the earlier studied azide^{4a,19a} and thiocyanate^{4a,19b} chromophores, which are not only their structural analogues but also electronic analogues from the point of view of localization and the nodal properties of the n and π^* orbitals participating in the first electronic transition.

Some deviation from planarity of the aldehyde, ketene, and diazo groups (Tables S-1 and S-2, Supporting Information) is observed in all fully and partially optimized structures of **1–9**. In ketenes **2**, **5**, and **8** and diazoalkanes **3**, **6**, and **9**, pyramidalization of the carbon C₁ and bending of the fragment C₁XY leads to the intrinsic chirality of the chromophore. However, because it remains essentially linear, the actual asymmetric deformation of the ketene/diazo chromophore is too small (Tables

(18) (a) Kirk, D. N.; Klyne, W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1076–1103. (b) Bouman, T. D.; Lightner, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3145–3154. (c) Lightner, D. A.; Bouman, T. D.; Wijekoon, W. M. D.; Hansen, A. E. *J. Am. Chem. Soc.* **1986**, *108*, 4484–4497. (d) Lightner, D. A.; Bouman, T. D.; Crist, B. V.; Rodgers, S. L.; Knobeloch, M. A.; Jones, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 6248–6259. (e) Lightner, D. A.; Crist, B. V.; Kalyanam, N.; May, L. M.; Jackman, D. E. *J. Org. Chem.* **1985**, *50*, 3867–3878.

(19) (a) Djerassi, C.; Moscovitz, A.; Ponsold, K.; Steiner, G. *J. Am. Chem. Soc.* **1967**, *89*, 347–352. (b) Djerassi, C.; Lightner, D. A.; Schooley, D. A.; Takeda, K.; Komeno, T.; Kuriyama, K. *Tetrahedron* **1968**, *24*, 6913–6933.

S-1 and S-2, Supporting Information) to make any significant contribution to the rotational strength.

The torsional dependencies of the $n-\pi^*$ rotational strengths of α,α -dimethyl substituted compounds **4–6** (Figure 4) are almost the same as could be predicted by adding the contributions of two α -monomethyl derivatives **1–3** displaced by 120° . In stable conformers *ss-4–6*, the mutual compensation of the contributions of the methyl groups lying in octants with opposite signs leads to the zero (for *ss-4*) or very low rotational strength (-0.10 for *ss-5* and -0.29 for *ss-6*). The same low rotational strengths are also observed for the other stable conformers of ketene **5** and diazoalkane **6**, i.e., *cs-5,6*. In these conformers, one of the methyl groups lies practically in the nodal plane and the other forms a dihedral angle of about 120° with the C_1X bond. At this angle, the contribution of the methyl group is also expected to be close to zero (Figure 3). By contrast, the methyl group of aldehyde **1** makes a significant positive contribution at a dihedral angle of 120° . Accordingly, almost the same positive rotational strength is calculated for *cs-4*.

As in the case of the *ss*-conformer of aldehyde **4**, contributions of the methyl and methylene groups in conformers *ss-7a–c* (Table 1) almost compensate each other. The rotational strength signs of these conformers are determined by a contribution of the terminal β -methyl group. In isomer *ss-7b*, this group is arranged close to a zigzag pattern and makes the consignate negative contribution. The β -methyl group in isomers *ss-7a* and *ss-7c* lying far away from the zigzag does not obey the octant rule. Since a perturbing influence of a β -substituent is smaller than one of an α -substituent, the rotational strengths of conformers *ss-7a–c* are several times smaller than the rotational strengths of *sc-7a–c* and *cs-7a–c*, in which the α -methyl or α -methylene group is the main perturber. The contributions of these groups obey the octant rule as was expected from the torsion dependency of the $n-\pi^*$ rotational strength of aldehyde **1** in the region of the dihedral angle about 120° (Figure 3). Thus, all isomers *sc-7a–c* are characterized by the positive rotational strengths (the α -methylene group in the left upper back octant) and all isomers *cs-7a–c* by the negative one (the α -methyl group in the left lower back octant). The signs and values of the rotational strengths of *sc*- and *cs*-isomers **7a–c** and their equilibrium populations are such that their contributions in the overall CE almost annihilate each other and the rotational strengths of isomers *ss-7a–c* themselves are fairly small. As a result, the theoretical average $n-\pi^*$ rotational strength of the equilibrium mixture of the isomers of aldehyde **7** is also small ($[R]_{av} = +0.6$ at 293 K). The sign of the this rotational strength is in agreement with the experimental one (Figure 6).

All calculated stable conformers of ketene **8** and diazoalkane **9** have mainly the smaller values of the $n-\pi^*$ rotational strengths in comparison with the corresponding conformers of aldehyde **7** (Tables 1–3). Such a result is predictable from the torsional dependencies of the rotational strengths of compounds **1–6** (Figures 3 and 4). Indeed, in a majority of the stable conformers of **8** and **9**, the α -methyl and α -methylene groups form with the CX bond the dihedral angles about 0° and 120° , where the perturbing influence of these groups is close to zero. In a few cases (*cs-8a*, *cs-8c*, *ss-9c*, and *sc-9a*), the values of these angles differ more significantly from 0° and 120° . In each case, the calculated signs of the overall $n-\pi^*$

rotational strengths of the equilibrium mixtures of ketene **8** ($[R]_{av} = +0.6$ at 260 K) and diazoalkane **9** ($[R]_{av} = +0.2$ at 293 K) are in accord with the signs of the first CE's in the CD spectra of these compounds (Figures 6 and 7). In addition, the signs of the CE's of the second (*n-3s*) transition at 240 nm and the third (*n-3p*) one at 223 nm as well as the relative intensity of all three CE's in the experimental CD spectrum of diazoalkane **9** (Figure 7) are reproduced well by the calculations: $[R]_{av} = +0.2$ ($n-\pi^*$), $[R]_{av} = -0.5$ (*n-3s*), $[R]_{av} = +2.7$ (*n-3p*).

Conclusions

1-Alken-1-ones (monoalkylketenes) and 1-diazoalkanes, as well as aldehydes, populate conformations with the CX double bond eclipsed by an α -substituent (α -hydrogen or α -alkyl group). The increase of the valence angle RCH and the narrowing of the angle RCX at the functional group RCH=XY and reduction of the electron acceptor ability of the C=X bond in the ketenes and diazoalkanes in comparison with the aldehydes led to the lowering of the rotational barriers of the functional group. For the same reasons, the global minimum of the ketenes and diazoalkanes is a conformer with the CX bond eclipsed by the α -hydrogen not by the α -alkyl group as in the case of the aldehydes. The greatest difference in conformational behavior is observed for the aldehydes and diazoalkanes; the ketenes occupy an intermediate position.

The influence of the α -alkyl substituent on the $n-\pi^*$ CE sign of the ketene/diazo chromophore obeys a reverse octant rule. In this respect, the ketene and diazo chromophores are entire analogues of the azide^{19a} and thiocyanate^{19b} chromophores. The obeying of the ketene/diazo chromophore to the reverse octant rule is limited within the region of the dihedral angles from 45° to 120° , which are formed by the α -alkyl perturber with the C=C/C=N bond. The maximum $n-\pi^*$ rotational strength is attained at the maximum overlapping of the perturbing $C_\alpha C_\beta$ bond with the π system of the functional group.

The low intensity of the $n-\pi^*$ CE of (*S*)-2-methylbutanal (**7**) is caused by the low optical rotational strength of the *skew-skew*-conformers and by mutual compensation of the contributions of the *skew-cis*- and *cis-skew*-ones. (*S*)-3-Methyl-1-penten-1-one (**8**) and (*S*)-2-methyl-1-diazobutane (**9**) are characterized by the even smaller intensities of the $n-\pi^*$ CE's because of an almost zero contribution of the α -alkyl perturber forming with the C=C/C=N bond the dihedral angle, which is close to 120° .

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Supporting Information Available: Tables S-1 and S-2 showing selected calculated geometrical parameters, dipole moments, and relative energies of the stationary structures of compounds **1–3** and **4–6** along with selected literature experimental data for aldehydes **1** and **4**. Table S-3 showing relative energies, $\Delta ZPVE$, and thermodynamic parameters (ΔS° , ΔH°) of the conformers of **7–9** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information

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