financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) through Grant 11-28-17. Financial support for the synthesis of d(GpTpG) was supplied by the Netherlands Organization for the Fight against Cancer. C. Erkelens is thanked for his assistance at the 300-MHz NMR facility of Leiden. Also F. J. Dijt, C. J. van Garderen, and Dr. G. W. Canters are thanked for the critical reading of the manuscript. The FPLC measurements were carried out at the Medical Biological Laboratory TNO (Rijswijk). Stimulating discussions with the group of Prof Dr. J. C. Chottard (Paris), made possible by the sponsorship of the French–Dutch cultural agreement, are gratefully acknowledged. We are indebted to Johnson Matthey Chemicals Ltd. (Reading, England) for their generous loan of K_2PtCl_4.

(π^* + σ^*) Molecular Orbital Mixing in β-Chloro Ketones and β-Chloro Olefins

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We have been interested in molecular orbital mixing of distal functionalities as a potential means of photochemically activating a normally UV transparent functional group.[1] For example, a C–Cl bond remote from, but propitiously placed with respect to, a π chromophore may be expected to create a LUMO which is (π^* + σ^*) and therefore potentially C–Cl labile in the excited state. Such mixing is well-known in α(axial)-halo ketones and has been invoked to rationalize the spectral perturbations[2] and photoreactivity[3] characteristic of these compounds. This report describes theoretical and exprimental results from our study of (π^* + σ^*) mixing in β-halo ketones and β-halo olefins.

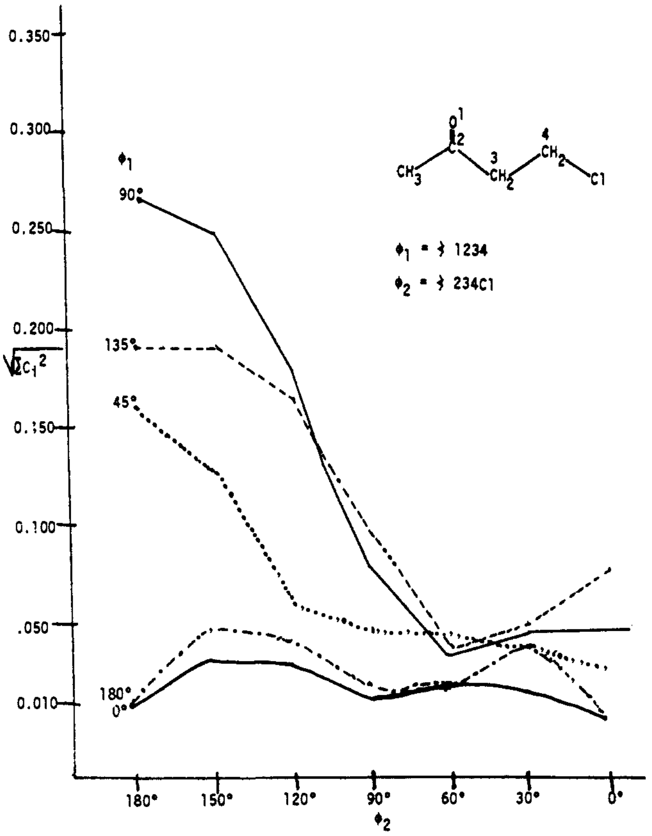

Figure 1. Relative amount of C–Cl involvement in the LUMO of 4-chloro-2-butanone as a function of the dihedral angles ϕ_1 and ϕ_2.

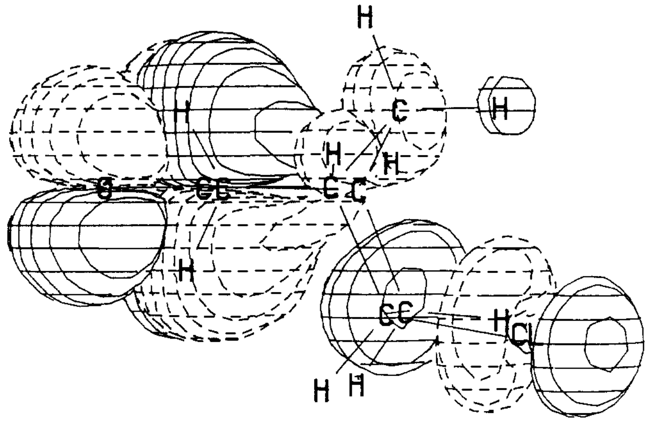

Figure 2. Contour plot of the LUMO of *exo*-6-chloro-2-norbornanone demonstrating both the π^* and σ^* components in this MO.

Table I. Relative (π^* + σ^*) Mixing in Representative Chloro Ketones[a]

chloro-1-cyclohexanone	orbital mixing	chloro-2-norbornanone	orbital mixing
2(a)-	1.00	1-	0.41
2(e)-	0.59	*exo*-3-	0.90
3(a)-	0.05	*endo*-3-	0.78
3(e)-	0.36	4-	0.19
4(a)-	0.04	*exo*-6-	0.53
4(e)-	0.32	*endo*-6-	0.06
		anti-7-	0.50
		syn-7-	0.13
		exo-5-	0.08
		endo-5-	0.13

[a] Orbital mixing values are $(\sum C_i^2)^{1/2}$ for C–Cl in the LUMO, normalized to 2(a)-chlorocyclohexanone. 4-Chloro-2-butanone: ϕ_1 = 90°; ϕ_2 = 180°; orbital mixing 0.51.

We initially calculated the degree of C—Cl/C=O mixing in the LUMO of the model substrate, 4-chloro-2-butanone, as a function of the dihedral angles, ϕ_1 and ϕ_2 (cf. Figure 1). Geometries were optimized by MNDO[4] and the wave functions calculated by using Gaussian 76[5] with an STO-3G basis set[6] (the relative degree of C–Cl involvement in the LUMO is represented by $(\sum C_i^2)^{1/2}$, where the $\{C_i\}$ run over the coefficients on Cl in this MO. It is evident from Figure 1 that C–Cl involvement is maximized when ϕ_1 = 90° and ϕ_2 = 180°, and in this conformation, the extent of mixing is about half of that calculated for axial 2-chlorocyclohexanone (cf. Table I). Such mixing is not unique to the ketone and, for example, a ca. 10% greater interaction is calculated for the olefin analogue 4-chloro-2-methylbutene. Table I includes data for other α, β-, and γ-chloro ketones and two entries are noteworthy: (1) equatorial, but not axial, 3-chlorocyclohexanone has an appreciable σ^* component in its LUMO, an observation consistent with the enhanced UV and CD absorption characteristic of such substrates;[2,7] (2) the greatest mixing for a β-chlorine is calculated for the *exo*-6- and *anti*-7-

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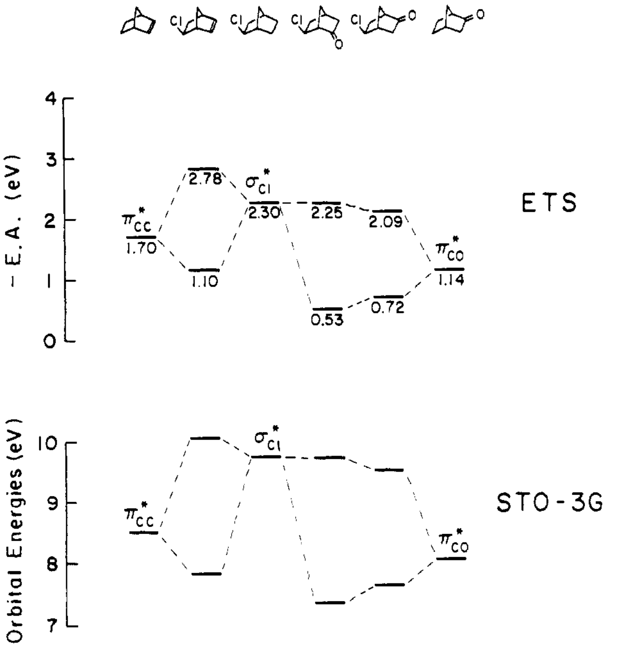

Figure 3. Experimental (ETS) EA's and theoretical energies of the virtual orbitals of *exo*-5-chloro-2-norbornene, *exo*-6-chloro-2-norbornanone, and reference compounds. The theoretical orbital energies were obtained from STO-3G calculations and application of Koopmans' Theorem.

chloro-2-norbornanones (cf. Figure 2), both of which stereoelectronically resemble the optimal 90°/180° conformation. The exo-6 isomer has been synthesized[9] and does indeed show marked bathochromicity and hyperchromicity in the HOMO → LUMO ("n → π^*") transition (e.g., λ_{max}^{MeOH} 300 nm (ϵ 68) vs. λ_{max}^{MeOH} 290 nm (ϵ 29) for norbornanone).

Electron transmission spectroscopy (ETS)[10,11] has proven particularly useful for directly observing changes in the energies of low-lying unoccupied orbitals as a result of orbital interactions.[11] For this reason we decided to employ ETS to study the interactions in *exo*-6-chloro-2-norbornanone and *exo*-5-chloro-2-norbornene, using as reference compounds *exo*-5-chloro-2-norbornanone, *exo*-2-chloronorbornane, norbornene and 2-norbornanone. The vertical electron affinities (EA) determined from the ET spectra and the orbital energies obtained from STO-3G calculations using Gaussian 82 are compared in Figure 3. In the context of Koopmans' Theorem the EA's may be associated with the negatives of the energies of unoccupied orbitals. Overall there is good agreement between the trends in the measured and calculated orbital energies. The β-chloro olefin ($\pi^* + \sigma^*$) interaction is clearly demonstrated in these results. The β-chloro ketone interaction is partially obscured by inductive effects which, for example, lower both the σ^* and π^* MO's in the γ-exo-5 isomer (for which orbital mixing is minimal, cf. Table I). Thus, the (π^* + σ^*) mixing in the exo-6 substrate is best seen by comparison with the exo-5 MO energies. A comparison of the ketone and olefin data confirms that ($\pi^* + \sigma^*$) mixing is appreciably greater in *exo*-5-chloro-2-norbornene than in *exo*-6-chloro-2-norbornanone.

Further studies on the spectroscopic and photochemical consequences of ($\pi^* + \sigma^*$) mixing between distal functionalities are in progress.

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Additions and Corrections

The Characterization of a New Heteropolytungstoarsonate Anion, $[CH_3AsW_7O_{27}H]^{7-}$. Topological Relationships among Ions Related to the Lindqvist Structure [*J. Am. Chem. Soc.* **1985**, *107*, 4911–4915]. GEOFFREY B. JAMESON,* MICHAEL T. POPE,* and SADIQ H. WASFI

Page 4911: The coauthors believe that the following ordering of names (S.H.W., M.T.P., G.B.J.) may reflect the contributions of the authors more accurately than that published (G.B.J., M.T.P., S.H.W.). In addition, an asterisk by S.H.W.'s name was inadvertently omitted in the galley proof.

Total Synthesis of (–)-Upial [*J. Am. Chem. Soc.* **1985**, *107*, 5570]. MICHAEL J. TASCHNER* and ABDULSADEH SHAHRIPOUR

Page 5570: The oxygen on the left hand side of structure **5** should be replaced by a $-CH_2-$.

Hexakis(2,4,6-triisopropylphenyl)cyclotristannane $(R_2Sn)_3$ and Tetrakis(2,4,6-triisopropylphenyl)distannene $(R_2Sn)_2$. Their

Unprecedented Thermal Interconversion and the First Solution Spectral Characterization of a Distannene [*J. Am. Chem. Soc.* **1985**, *107*, 6390–6391]. SATORU MASAMUNE* and LAWRENCE R. SITA

Page 6391, left column: 2.18 × 10^{-3} M (at 50 °C, in the 8th line from the bottom, and 70 °C, in the 7th line from the bottom, should read 3.81 × 10^{-4} M (at 70° C and 50 °C, respectively. These corrections are necessitated by our earlier erroneous transcription of the original data and do not affect the statements made in the communication.

Thiamin Biosynthesis in *Saccharomyces cerevisiae*: Origin of the Pyrimidine Unit [*J. Am. Chem. Soc.* **1986**, *108*, 146–158]. GUNNAR GRUE-SØRENSEN, ROBERT L. WHITE, and IAN D. SPENSER*

Page 149: The first sentence in the Discussion should read as follows—The circumstantial evidence which was reviewed in the introduction, ...