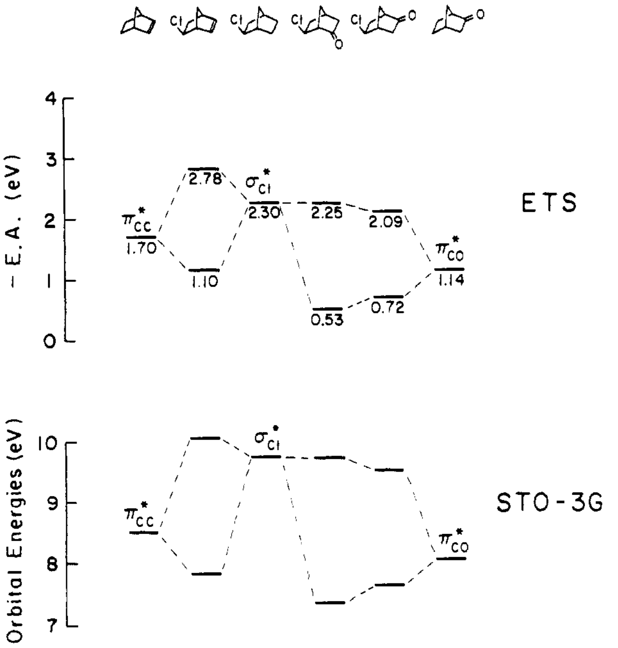

**Figure 3.** Experimental (ETS) EA's and theoretical energies of the virtual orbitals of *exo*-5-chloro-2-norbornene, *exo*-6-chloro-2-norbornanone, and reference compounds. The theoretical orbital energies were obtained from STO-3G calculations and application of Koopmans' Theorem.

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 → $\pi^*$") transition (e.g., $\lambda_{max}^{MeOH}$ 300 nm ($\epsilon$ 68) vs. $\lambda_{max}^{MeOH}$ 290 nm ($\epsilon$ 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 $\beta$-chloro olefin ($\pi^*$ + $\sigma^*$) interaction is clearly demonstrated in these results. The $\beta$-chloro ketone interaction is partially obscured by inductive effects which, for example, lower both the $\sigma^*$ and $\pi^*$ MO's in the $\gamma$-exo-5 isomer (for which orbital mixing is minimal, cf. Table I). Thus, the ($\pi^*$ + $\sigma^*$) 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, ...