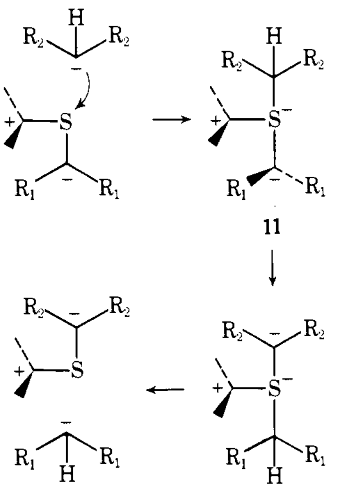
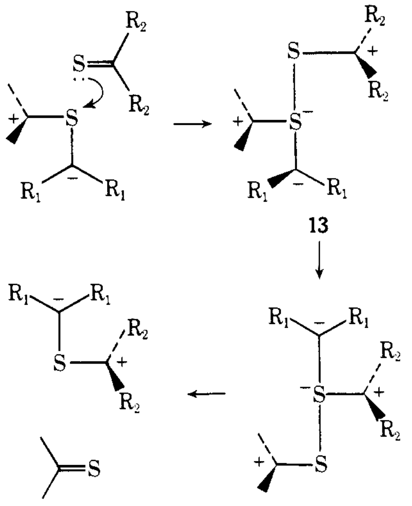


bis(dimethylamino)-substituted ylides.[7] This process, which is equivalent to ligand transfer between ylide and thione, appears to proceed in a direction to provide the ylide with the less effective π-electron donor substituents. Rationalizing this behavior in a manner consistent with the other observed multiple ligand exchange and displacement reactions requires an intermediate **13** in which the equivalent of a 1,2-shift of the π-electron rich group occurs to give **14**; the driving force for the shift is dictated by the formation of the most stable sulfurane as determined by the electron withdrawing ability of the equatorial substituent. In conclusion, the general features of the chemistry of highly perturbed thione methylides closely resemble those of sulfuranes and are certainly unlike those of the unperturbed congeners.



Acknowledgments. We sincerely wish to thank the National Institutes of Health, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for research grants.

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(15) The calculated composition of π-LUMO at sulfur is $0.1508p_y - 0.1947d_{xy} - 0.0567p_x$ and the resultant hybrid is shown in Figure 1.

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The Structure of a Substituent Stabilized Thione Methylide

Sir:

The pericyclic chemistry observed for 1,3-dipolar ylides ($R_2C{=}X^+{-}C^-R_2$) containing certain first-row central atoms (X = N, O) has been correlated using the occupied π-molecular orbitals associated with an "allyl anion" bonding model requiring a planar geometry for the substituted ylide.[1] Extension of this model to define the stereochemistry of second-row (X = S) symmetrically substituted thione methylide electrocyclic closures to thiiranes has been successful.[2] The potential surface for conrotation of a thione methylide (**1**) to thiirane (**2**) is to the first approximation dependent upon the energetic behavior of key high-lying molecular orbitals as determined by symmetry conservation (Woodward-Hoffman).[3] The alteration of this surface by a large deviation from symmetry could possibly provide intermediates of lower energy than either end-point reactant as well as change the preference for a particular ring closure mode as indicated by a recent theoretical investigation.[4] Snyder has calculated the shape of the one-dimensional surface (Figure 1) for the conversion of an unperturbed symmetric planar thione methylide, **1a**, to the corresponding thiirane **2a**, using a conrotatory motion (the forbidden disrotatory transition state lies > 7 kcal/mol above the allowed one) in agreement with the observed stereochemistry.[3] We have examined this analogous surface for the closure of an asymmetric thione methylide **1b** perturbed with π-donor

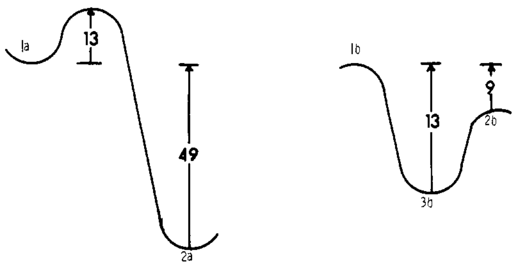


Figure 1. Potential surfaces for the conversion of unperturbed (right) and perturbed (left) thione methylides to thiiranes. The energy differences are shown in kilocalories per mole.

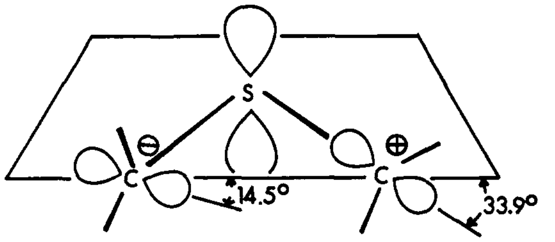
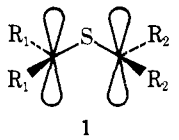


Figure 2, π-Orbital topology of **5a**.

Table I. NMR Chemical Shifts in **5** Relative to Me_4Si in Me_2SO-d_6

	Chemical shift (δ)		
Compound	H_a	C_a	C_b
5c	7.81	144.2	9.9
5b	7.69	144.1	34.5
5a	7.51	146.1	59.1

(R_1) and acceptor (R_2) substituents using an energy-geometry optimized SCF-MINDO3 procedure.[5] The results (Figure 1) reveal a striking departure from the unperturbed system with both end-point structures of higher energy than a nonplanar intermediate, **3b**. The local surface in the vicinity of **3b** is reasonably flat with rotamers such as **4b** lying only 1.4 kcal/mol above **3b** and configuration interaction with the first doubly excited state lowered but failed to reorder these energies.[6] The critical molecular orbital whose energy contributes most to reordering the total calculated energy of the planar ylides, **1a** and **1b**, relative to their respective nonplanar conrotated transition state or intermediate structures is the highest occupied molecular orbital, π_2. The substituent perturbation on this orbital shifts the node toward the π-acceptor substituted carbon thus increasing the electron density on sulfur and raising in π_2 the antibonding character relative to the symmetric structure. The small total energy separation of **3** and **4** is derived from the difference that the π-donor substituted carbon p_π-orbital experiences upon interaction with either the in or out-of-plane sulfur lone pair orbital. With the above theoretical analysis in mind it would be of interest to examine the structure of a substituent-perturbed thione methylide available from previous synthetic efforts,[7] and we now wish to report the details of such a study. Due to its high thermal stability ylide **5a** was selected for an x-ray crystallographic analysis.[8] The C_aSC_b angle is an unexceptional 104.26° while the C_aS and C_bS lengths are both 1.7 Å and thus intermediate between a CS double and single bond, as has been observed for 1,2-sulfonium methylides.[9] However, the most extraordinary feature is the inclination of the C_a and C_b substituent planes to the C_aSC_b plane which results in a carbon p_π-orbital topology as shown in Figure 2, and the close correspondence to the theoretically derived structures **3–4** is notable.



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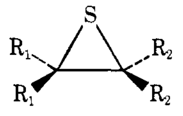

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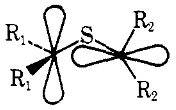
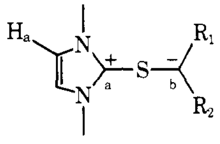


3

4

a, $R_1,R_2 = H$
b, $R_1 = N(Me)_2$; $R_2 = CHO$



5a, $R_1,R_2 = CO_2Et$
b, $R_2 = CN$; $R_2 = CO_2Me$
c, $R_1,R_2 = CN$

Some conclusions as to the role of a cental second-row atom in conjugative interaction between the carbon termini in 1,3-dipolar ylides may be drawn from magnetic resonance spectroscopy studies. The efficiency of charge transmission across the methylide sulfur atom is evident from the effect of various combinations of electrons withdrawing substituents at C_b on selected ^{13}C and ^1H NMR chemical shifts in the system **5** (Table I). A correlation appears to exist between the ring current induced diamagnetic anisotropic deshielding of H_a with the degree of total shielding of C_b while the relative shifts of C_a remain small and consistent with the view that ring current variations have little effect on ^{13}C shifts.[10] To further identify the mode (σ vs. π) of charge transmission in perturbed thione methylides the $^{13}C_a$ shift of **6** was compared with some reference compounds, **7** and **8** (Table II). The calculated values shown in Table II were based upon the following assumptions: (a) the dominant contribution to the differences in chemical shift were nearest neighbor dependent and derived from variations in the second-order paramagnetic shielding tensor, $\sigma_{xyz}{}^{(2)}$, for the 2p orbitals of C_a, (b) the mean excitation energy, ΔE, was localized at C_a-S and could be approximated by the calculated n_s,π^* transition,[11] and (c) the largest variation in the rotationally averaged second-order term arose essentially from $\sigma_z{}^{(2)}$ of the carbon p_π-orbital. Using the Karplus-Pople relationship,[12] $\sigma_z{}^{(2)} \cong [-e^2h^2/48m^2c^2a_0{}^3][3.25 - 0.35\ (P_{ii} - 1)]^3[P_{ii} + \Sigma_jP_{ij})/\Delta E]$, and the diagonal ($P_{ii}$) and off-diagonal ($P_{ij}$) density matrix elements as well as ΔE from a SCF-CNDO2 calculation[13] for C_a in **6**, 7, and **8**, the calculated values were fitted to a line, $\sigma_{xyz}{}^{(2)} = 1.0383\sigma_z{}^{(2)} - 1.6$ ppm. A planar geometry was assumed for **8** but **6** was allowed to adopt the three-dimensional structure found for **5a**. With inclusion of sulfur d orbitals in the basis, the order of calculated ^{13}C shifts is the same as the observed values; no correspondence between the C_a orbital electron population (P_{ii}) or the bond orders (P_{ij}) and this observable are apparent. However, the C–S bond order when scaled by the overlaps (S_{ij}) to represent its contribution to the total Mulliken population[14] does correlate with the observed shifts. Although such a population analysis is at best approximative it does seem to qualitatively indicate a CS partial double bond providing the stabilizing conjungative link between the two charged centers

$(Me_2N)_2C^+{}_aSC^-(CO_2Et)_2$

6

$(Me_2N)_2C_a{=}S$ **7** $\quad (Me_2N)_2C^+{}_aSMe\ I^-$ **8**

Table II. Observed $^{13}C_a$ Chemical Shifts (relative to Me_4Si) and Calculated Parameters

Compounds	δ(obsd)	$\sigma_{xyz}{}^{(2)}$	$\sigma_z{}^{(2)}$	P_{ii}	Σ_jP_{ij}	$P_{ij}S_{ij}$
7	−193.9	−190.9	−185.4	0.6822	1.4542	0.1446
6	−180.8	−182.5	−177.3	0.7509	1.1554	0.1076
8	−174.5	−175.6	−170.7	0.6811	1.4294	0.0684

through sulfur. The inclusion of higher-order d orbitals of proper symmetry in the sulfur basis for the orbital description no doubt leads to more favorable charge distribution (increased electron density at the electropositive sulfur) due primarily to modification of the nonbonding π-orbitals. The bonding contribution of d orbitals to the actual total energy of such sulfur compound is controversial. The net lowering of the calculated SCF energy with a d-orbital inclusive basis may not be due to a net decrease in the occupied orbital energies but a result of altered Coulomb and exchange terms.[15]

Acknowledgments. We sincerely wish to thank the National Institutes of Health, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for research grants.

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(6) The optimized CSC angles found for **1a**, **3a**, and **4a** were 137.3° 126.3°, and 123.3°. Forced rotation in **4a** of the π-acceptor substituted carbon p-orbital out of the CSC plane resulted in a rapid increase in the heat of formation accompanied by an equal (optimized) *conrotation* of the π-donor substituted carbon p-orbital. This would seem to indicate that the stereomode of conversion of 1 → 2 follows the Woodward-Hoffmann rules even *in a highly perturbed system.*

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Mechanistic Photochemistry of β,γ-Unsaturated Ketones. An Alternative Excited State Assignment for the 1,3-Acyl Shift Reaction of Alkyl β,γ-Enones

Sir:

The photochemistry of β,γ-unsaturated carbonyl compounds is continuing to generate considerable interest.[1,2] Part of the appeal of these bichromophoric molecules is the dichotomy often observed between the results of direct and sensitized irradiations.[1,2] Detailed understanding of the factors that govern the chemical reactivity of β,γ-enone excited states requires definitive knowledge of which excited states are responsible for the various photoprocesses observed.

The 1,3-acyl shift reaction which often occurs on direct irradiation of β,γ-enones has been universally assigned for alkyl β,γ-unsaturated ketones as a $^1n,\pi^*$ (S_1) reaction.[1,2] The primary basis for this assignment has been the observations that the 1,3-acyl shift of alkyl β,γ-enones is not quenched by triplet quenchers and that sensitized irradiation of these ketones usually yields only processes such as 1,2-acyl shifts and cis-trans isomerization, which are not commonly observed on direct irradiation. There seems to be little doubt that these sensitized reactions occur from the T_1 state which for alkyl β,γ-unsaturated ketones is primarily π,π^* in character.[2a] Houk has attributed the differing reactivity of the S_1 and T_1 states of alkyl β,γ-enones to the n,π^* character of S_1 and the π,π^* character of T_1.[2a,3,4] This explanation is consistent with the fact that β,γ-unsaturated carbonyl compounds with n,π^* T_1 states, e.g., aromatic β,γ-unsaturated ketones and β-diketones, often undergo 1,3-acyl shift reactions originating from the T_1 state.[2] We report results which suggest that at least for some alkyl β,γ-enones, the 1,3-acyl shift observed on direct irradiation is occurring from the $^3n,\pi^*$ T_2 state rather than the $^1n,\pi^*$ S_1 state.

We were initially prompted to question the universal assignment of the 1,3-acyl shift reaction of alkyl β,γ-enones to the $^1n,\pi^*$ state by (a) the observation of fluorescence from both β,γ-enones which are reactive and β,γ-enones which are unreactive toward the 1,3-acyl shift;[1e,5] (b) the fact that 1,3-acyl shifts are often unable to compete with intramolecular γ-hydrogen abstraction from the β,γ-enone $^1n,\pi^*$ state;[1f,j,m,2a,6] and (c) reports that the use of high energy sensitizers, e.g., acetone, sometimes results in sensitized, albeit inefficient, 1,3-acyl shift reactions of alkyl β,γ-unsaturated ketones.[1l,m,2a,6d,7] The observations indicate that 1,3-acyl shift reactions can occur from triplet states of alkyl β,γ-enones, and are difficult although not impossible to explain if the 1,3-acyl shift observed on direct irradiation of alkyl β,γ-enones is solely a $^1n,\pi^*$ state reaction. These problems become significant when it is realized that nothing presently known about the 1,3-acyl shift reaction of alkyl β,γ-enones rules out the possibility that it is occurring from T_2, an upper triplet state predominantly n,π^* in character,[2a,3] located a few kilocalories per mole above the π,π^* T_1 state,[2a,11] and too short-lived to allow triplet quenching. Reaction from T_2 ($^3n,\pi^*$) would readily explain both the apparent lack of competition of the 1,3-acyl shift with S_1 processes (fluorescence and intramolecular γ-hydrogen abstraction) and the occasional observation of sensitized 1,3-acyl shift reactions when high energy sensitizers, which may be capable of transferring energy to T_2, are used. In addition, 1,3-acyl shift reaction from the β,γ-enone $^3n,\pi^*$ state is consistent with (a) Houk's calculations[2a,3] on reactivity as a function of excited state configuration; (b) the much greater reactivity of alkanone $^3n,\pi^*$ states than $^1n,\pi^*$ states toward α-cleavage processes;[8,9] and (c) the observation of triplet 1,3-acyl shift reactions from β,γ-unsaturated ketones with lowest n,π^* triplet states.[2a]

If the 1,3-acyl shift is occurring from T_2, then β,γ-enones, which on direct irradiation yield a 1,3-acyl shift but no T_1 photoproducts, must undergo reaction from T_2 at a rate much faster than the rate of internal conversion from T_2 ($^3n,\pi^*$) to T_1 ($^3\pi,\pi^*$).[10] Processes other than internal conversion are observed only rarely from upper triplet states.[11] 1,3-Acyl shifts from T_2 seem conceivable for some alkyl β,γ-unsaturated ketones, however, given that (a) β,γ-enone $^3n,\pi^*$ states, particularly for α-alkyl substituted β,γ-enones, should be very reactive toward α-cleavage processes,[12] and (b) internal conversion in alkyl β,γ-enones from a $^3n,\pi^*$ T_2 state to a $^3\pi,\pi^*$ T_1 state may be slower than normal T_2 to T_1 internal conversion to the extent that the two states are localized on different nonconjugated chromophores.[13,14]

In order to gain further insight into whether the 1,3-acyl shift observed on direct irradiation of alkyl β,γ-enones is a $^1n,\pi^*$ S_1 reaction or a $^3n,\pi^*$ T_2 reaction, we have embarked upon a detailed study of the efficiency (Φ_f) and lifetime (τ_f) of the fluorescence of β,γ-unsaturated ketones, including both enones which are "reactive" and enones which are "unreactive"