increasing catalyst turnovers, even though the 20.5-Å basal spacings are retained.

In summary, our new chromia pillared clays exhibit gallery heights (11.7 Å after dehydration at 500 °C) that are ~3.0 Å larger than those of zirconia and alumina pillared clay catalysts. The scope of their intracrystalline catalytic and sorptive properties, along with structural studies of the intercalated chromia aggregates, are under active investigation and will be the subjects of future reports.

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Registry No. Cyclohexane, 110-82-7; chromia, 1308-38-9.

Dynamic NMR Study of Phenyl Thiolformate. Nonaromaticity of the *Z* Conformation[1]

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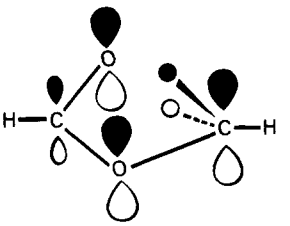
The interaction in amides, esters, and thiol esters between a lone pair of electrons on the heteroatom and π^* of the carbonyl group stabilizes the planar conformations, and most of these compounds are planar or nearly planar.[2] Esters of carboxylic acids generally have a strong preference for the conformation in which the alkyl group attached to the "ether" oxygen is cis to the carbonyl oxygen.[3,4] The corresponding (*Z*) conformation of secondary amides is also generally of lower energy than the *E* isomer,[5] and this preference is of importance in determining the conformations of proteins.

In compounds such as methyl acetate, steric repulsion in the *E* conformation between the alkyl groups is expected to favor the *Z* conformation. However, the *E* isomer of methyl formate contributes only 0.3% to the conformational mixture at −83 °C in DMF/acetone-d_6 solvent,[6] corresponding to a free energy difference of 2.2 kcal/mol, although any steric repulsion between the methyl group and formyl hydrogen in this conformation should be more than offset by repulsion between the methyl group and the larger carbonyl oxygen in the *Z* isomer. Indeed, the free energy difference for *tert*-butyl formate is smaller (0.5 kcal/mol),[6] but the equilibrium still favors the *Z* isomer. Thus, steric repulsion between the two alkyl groups in acetates and higher esters may reinforce the conformational preference that exists in formate esters but cannot entirely account for the conformational preferences in these compounds.

A number of possible explanations for the lower energy of the *Z* conformation of esters have been proposed,[7] three of these are probably important for methyl formate: (1) Dipole–dipole interactions destabilize the *E* conformation, relative to the *Z*, as indicated by the dipole moments of the two conformations of formic acid.[9] (2) Interaction of the "ether" oxygen lone pair with σ^* of the carbonyl group of the *Z* conformation may stabilize this isomer.[8] (3) A cyclic "aromatic" system of six electrons is possible for the *Z* conformation,[10] with the carbonyl group, the "ether" oxygen, and the methyl group[12] each contributing two electrons, as indicated below. A similar stabilizing interaction is not possible for the *E* isomer.



The first two factors should be of lower importance for thiol esters than for esters. The dipole moments for the two conformations of thiolformic acid differ by 1.3 D,[13] while the corresponding difference for formic acid is 2.4 D,[9] indicating that dipole–dipole repulsion will be more important in decreasing the population of the *E* conformations of carboxylic acids and esters than for the related sulfur compounds. A CXC bond angle of 90° in RCO(XR′) would leave one lone pair of electrons in an s orbital and the other pair in a p orbital. The electrons of the p orbital could not interact with σ^*, and any interaction of the remaining lone pair with σ^* should be of nearly equal importance for either conformation. The smaller CSH bond angle for (*Z*)-thiolformic acid (92.7°)[14] than for the COH angle of (*Z*)-formic acid (106.8°)[15] suggests that the n–σ^* interaction may be lower for thiolformic acid.

The position of equilibrium for a thiol ester in solution should then be influenced mainly by the "aromaticity" of the *Z* isomer.[16]

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(3) For the esters discussed here, this conformation will be the *Z* isomer. For compounds such as methyl fluoroformate, the conformational designations would be reversed.

(4) For a review, see: Jones, G. I. L.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 1.

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(6) Grindley, T. B. *Tetrahedron Lett.* **1982**, *23*, 1757.

(7) For a summary, see ref 8.

(8) Larson, J. R.; Epiotis, N. D.; Bernardi, F. *J. Am. Chem. Soc.* **1978**, *100*, 5713.

(9) (*E*)-Formic acid, μ = 3.79 D; (*Z*)-formic acid, μ = 1.420 D. Hocking, W. H. *Z. Naturforsch., A* **1976**, *31A*, 1113.

(10) For a discussion of aromaticity in (*Z*)-methyl vinyl ether, see: Bernardi, F.; Epiotis, N. D.; Yates, R. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 2385. The importance of aromaticity or antiaromaticity in other systems has been noted by: Cremer, D.; Binkley, J. S.; Pople, J. A.; Hehre, W. J. *Ibid.* **1974**, *96*, 6900. A nonbonded attraction has been suggested for the *Z* conformations of methyl formate and related compounds[11a] and for (*Z*)-methyl nitrite.[11b] A number of compounds, including esters and amides, have been discussed in detail by: Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1.

(11) (a) Lister, D. G.; Palmieri, P. *J. Mol. Struct.* **1976**, *32*, 355. (b) Cordell, F. R.; Boggs, J. E.; Skancke, A. *Ibid.* **1980**, *64*, 57.

(12) For a description of the π-type orbitals of a methyl group, see: Hoffman, R.; Radom, L.; Pople, J. A.; Schleyer, P. von R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.*, **1972**, *94*, 6221.

(13) (*E*)-Thiolformic acid, μ = 2.87 D; (*Z*)-thiolformic acid, μ = 1.54 D. Hocking, W. H.; Winnewisser, G. *Z. Naturforsch., A* **1976**, *31A*, 995.

(14) Hocking, W. H.; Winnewisser, G. *Z. Naturforsch., A* **1976**, *31A*, 438.

(15) Bellet, J.; Deldalle, A.; Samson, C.; Steenbeckeliers, G.; Wertheimer, R. *J. Mol. Struct.* **1971**, *9*, 65.

(16) The acidic proton of a thiol acid cannot complete an aromatic sextet in the *Z* conformation, and we have observed both conformations of thiolacetic acid using low-temperature NMR.[17] Kalinowski et al.[18] have reported populations of 0.525 and 0.475 for the *E* and *Z* conformations of thiolformic acid at −113 °C in CD_2Cl_2 solution. However, the room-temperature chemical shifts reported by these authors (δ 7.88 and 2.32) differ markedly from the values of δ 10.18 and 4.66 obtained by Engler and Gattow[19] for a solution in $CDCl_3$. In a preliminary study of thiolformic acid, we have found chemical shifts above coalescence of δ 10.3 and 5.1, indicating that the values of ref 18 are in error by more than 200 Hz. Our preliminary study has qualitatively confirmed that both conformations are appreciably populated at low temperatures. Populations of 0.25 (*E*) and 0.75 (*Z*) at 27 °C were obtained[13] from a microwave study of thiolformic acid in the gas phase.

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(18) Kalinowski, H. O.; Hocking, W. H.; Winnewisser, B. P. *J. Chem. Res., Synop.* **1978**, 260.

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Only the *Z* conformation of methyl thiolformate was found[2c] in the gas phase by microwave spectroscopy, and the similarity of the dipole moments in benzene (1.6 ± 0.1 D)[2c] and in the gas phase (1.58 ± 0.05 D)[2c] indicates that the *Z* conformation also predominates in the solution. We have found from a DNMR study of *tert*-butyl thiolformate in $CHClF_2/CHCl_2F$ (2:1) that the *Z* conformation also predominates in this compound (85% at −105 °C).[20] The phenyl group of phenyl thiolformate (**1**) cannot complete an aromatic sextet of the *Z* conformation, and it was expected that the *E* isomer of this compound would be appreciably populated in solution.

The NMR spectrum (90.02 MHz) of **1** in $CHClF_2/CHCl_2F$ (2:1) at +25 °C shows a single peak for the formyl proton at δ 10.16. At lower temperatures, the peak broadens and splits into two lines at δ 10.07 and 10.21, with populations of 0.60 and 0.40, respectively, at −104 °C.[21] A free-energy difference at this temperature of 0.13 kcal/mol was calculated from the relationship $\Delta G° = -RT \ln K$, and populations of 0.58 and 0.42 were estimated at the coalescence temperature (−80 °C), assuming that $\Delta G°$ does not change with temperature. Rate constants of 17 s^{-1} ($Z \rightarrow E$) and 23 s^{-1} ($E \rightarrow Z$) were obtained by comparison of the experimental spectrum at coalescence with theoretical line shapes[22] generated for different rate constants, and the corresponding free-energy barriers were calculated from the Eyring equation (10.1 ± 0.2 and 9.9 ± 0.2 kcal/mol at −80 °C).

Although steric interactions in planar **1** should destabilize the *Z* conformation, some evidence suggests that the phenyl group may actually be perpendicular to the rest of the molecule, and therefore the difference in steric interactions for the two conformations is probably small. The rotational barrier of thiophenol is only 0.8 kcal/mol, favoring the planar form,[23] while the resonance interaction for the lone pair and the phenyl group can be estimated[24] as $33|\sigma_R°| = 33(0.19)[24] = 6.3$ kcal/mol. Much of the difference between the resonance energy and the rotational barrier is probably due to stabilization of the transition state by interaction of an occupied orbital of the phenyl group with σ* of the SH bond.[25] Support for this interpretation comes from the effects of adding an electron to the benzene ring to form the radical anion[25] or adding an amino group in the para position;[26] in both cases, the perpendicular conformation is stabilized and becomes the preferred conformation. In phenyl thiolformate, the cross conjugation of the sulfur lone pair with the carbonyl group should make the sulfur a poorer π-donor to the benzene ring than in thiophenol and should also favor the perpendicular conformation. The *R* value for the CH_3COS group (+0.68)[27] is consistent with a nonplanar and possibly perpendicular orientation for phenyl thiolacetate and, by extension, for the thiolformate ester.

The available evidence then indicates that the phenyl group in **1** is not coplanar with the rest of the molecule[28] and that the small energy difference between conformations is due to the lack of aromaticity of the *Z* isomer, rather than to steric interactions. The percentage of the *E* isomer in *N*-phenylformamide is also high (27–55%),[5] compared to *N*-methylformamide (8%),[29] although the conformational equilibrium in this system will be affected by hydrogen bonding, and steric effects may also be important.

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(21) The low-field/high-field peak area ratio increases in acetone-d_6 as solvent, indicating that the low-field peak is associated with the more polar *E* isomer.

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(28) Other evidence includes the relative barriers for **1** (9.9 and 10.1 kcal/mol) and for *tert*-butyl thiolformate in the same solvent (9.0 and 9.6 kcal/mol). The higher barriers for **1** suggest that the sulfur lone pair in this compound is not effectively cross conjugated with the phenyl group. The formyl proton of (*E*)-phenyl thiolformate absorbs at substantially higher field than for (*E*)-*tert*-butyl thiolformate (δ 10.21 vs. 10.73), while the corresponding difference is much smaller for the *Z* conformations (δ 10.07 vs. 9.97), with the *tert*-butyl compound absorbing at slightly higher field. A referee has noted that the upfield shift of the formyl proton of (*E*)-phenyl thiolformate is consistent with the proposed conformation; if the phenyl group in **1** is perpendicular to the plane of the formyl group, the formyl hydrogen should lie in the shielding region of the benzene ring. A comparison of the populations of the *E* isomers (0.40 and 0.15) and the barriers of **1** and *tert*-butyl thiolformate indicates that a steric effect is not a major factor in destabilizing the *Z* conformation of **1**. Phenyl thiolformate has both a higher population of the *E* conformation and higher rotational barriers. If the steric effect of the phenyl group were larger than for *tert*-butyl, the barriers for **1** would be expected to be *lower* than for *tert*-butyl thiolformate, as a consequence of destabilization of the planar ground states.

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General Approach for the Synthesis of Polyquinenes.[3] 2. Synthesis of Tetracyclo[5.5.1.$0^{4,13}$.$0^{10,13}$]tridecane-2,5,8,11-tetraene

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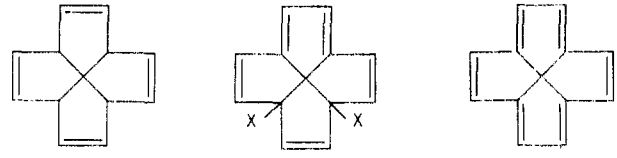
Tetracyclo[5.5.1.$0^{4,13}$.$0^{10,13}$]tridecane-2,5,8,11-tetraene (**1**) has



1 **2**, X = H, or Br **3**

been a target of considerable interest to organic chemists for some time.[4-7] This stems, in part, from the desire to study the stability

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(2) National Institute of Arthritis, Diabetes, Digestive and Kidney Diseases.

(3) For part 1 in this series, see: Venkatachalam, M.; Jawdosiuk, M.; Deshpande, M.; Cook, J. M. *Tetrahedron Lett.* **1985**, *26*, 2275 and references cited therein.

(4) The structure of **1** appears on the inside front cover of: Hendrickson, J.; Cram, D. J.; Hammond, G. "Organic Chemistry", 3rd ed.; McGraw Hill: New York, 1970. The tetraene **1** is contained in an assembly of compounds of theoretical interest of which only a few have been synthesized, including cubane (Eaton) and dodecahedrane (Paquette).

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