ψ_2° and ψ_3° gives the predominant contribution to the total electronic asymmetry. Examination of the product $\psi_2^\circ\psi_3^\circ$ at the substitution sites easily shows that molecule II (product with same sign on the two substituents) has a larger asymmetry than molecule I (different sign).

More generally, in an alternant hydrocarbon, the asymmetry will be largest if the substituted atoms all belong to the same set ("starred", or "unstarred").[3] Two typical substitution patterns for hexatriene are shown, where molecule III has a small total asymmetry and molecule IV a large total asymmetry.
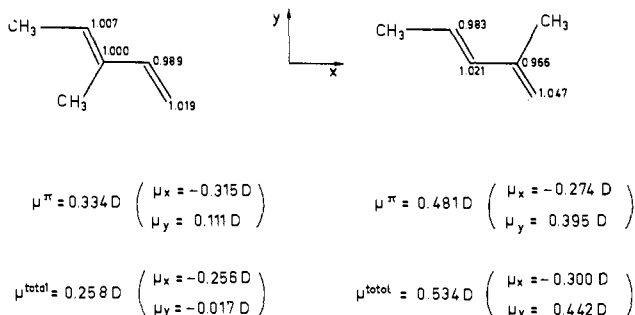

III   IV
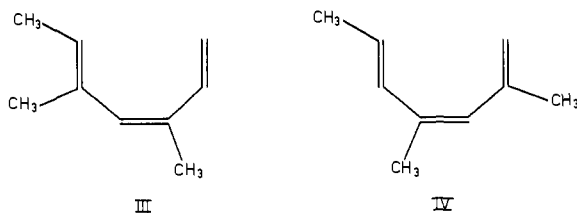
A first experimental test of these predictions can be made with the dipole moment. The calculated (ab initio, STO-3G) π-charge distribution[4] and the π and total dipole-moment components are shown in Scheme II for the molecules in their equilibrium trans conformation. The calculated total dipole moments are mostly due to the π-system polarization. Furthermore, the contribution μ^π to the overall dipole is much larger in II than in I, whose dipole would be practically 0 were it not for the methyl contribution.[5] The larger observed dipole in II vs. I (0.62 D vs. 0.58 D),[6] although it confirms nicely our prediction of a larger electronic asymmetry in II, reflects only very partially the extent of the difference in electronic asymmetry.

Electronic asymmetry should also have a bearing on the rate of pericyclic reactions.[7] For instance one might expect the concerted conrotatory motion to be slightly less facile in II than in I, or the disrotatory motion to have a slightly lower activation barrier. Preliminary calculations however do not seem to support this hypothesis, since no significant (>1 kcal/mol) activation energy difference is found in either process between I and II.

The asymmetry should also affect the *regioselectivity* of cycloadditions in which the asymmetric molecule is a partner. One might expect the regioselectivity to be greater the greater the electronic asymmetry. The regioselectivity of 1-methyl-butadiene is larger than that of 2-methylbutadiene,[8] in agreement with the larger total asymmetry induced by substitution at the C_1 atom (the mixing coefficient between ψ_2° and ψ_3° is larger in the 1-methyl compound). To our knowledge, the addition of dissymmetrical olefins to 1,2-disubstituted butadienes has not yet been studied, but the experimental obser-

vations on monosubstituted dienes[8] indicate that the directing effects of the substituents should add in II and cancel in I, in agreement with the larger electronic asymmetry of II.

References and Notes

(1) Nothing forbids *S*,*S* or *A*,*A* mixings: for instance, for single substitution.
(2) The same result is obtained by perturbation theory, which requires ground-state wave function to mix with excited wave function.
(3) L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, N.Y. 1966, p 36.
(4) In both molecules, there is a slight incremental π charge, due to hyper-conjugation, of 0.015 e⁻.
(5) In the *anti*-1,2-dimethylbutadiene, the dipole moment is much smaller than in the syn isomer I (0.098 D vs. 0.258 D). Therefore, the dipole moment in I is mostly due to the syn orientation of the methyl groups.
(6) These values are averages of gas phase and solution measurements: (a) N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.*, **68**, 244 (1946); (b) E. H. Farmer and F. L. Warren, *J. Chem. Soc.*, 1302 (1933).
(7) R. Breslow, J. Napierski, and A. H. Schmidt, *J. Am. Chem. Soc.*, **94**, 5906 (1972).
(8) J. Sauer, *Angew. Chem., Int. Ed. Engl.* **6**, 16 (1967). The consideration of the asymmetry of the HOMO alone leads to the opposite prediction.[9]
(9) O. Eisenstein, J. M. Lefour, Nguyen Trong Anh, and R. F. Hudson, *Tetrahedron*, **33**, 523 (1977).

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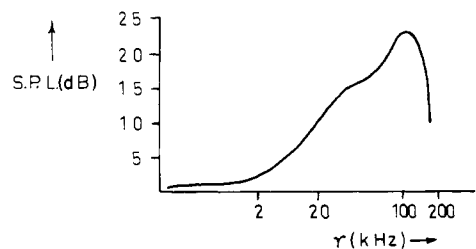## Acoustic Emission during the Preparation of Dichloro(pyrazine)zinc(II)

Sir:

As part of an investigation on linear-chain compounds, having potentially bridging ligands, an unusual acoustic effect was noticed during the synthesis of the title compound. Upon addition of a solution of $ZnCl_2$ (1 mol/L) in water to a solution of pyrazine (1 mol/L) in water, immediately a precipitate is formed. This precipitation is accompanied by a rather strong cracking sound. This cracking is heard again when the mixture is shaken after some hours. The intensity of this acoustic emission appeared to be proportional to the concentrations of both the reactants; the higher the concentration, the louder the cracking. A temperature increase accompanies these crackings, which is stronger than the rise in temperature observed upon dilution of concentrated aqueous $ZnCl_2$ solutions.

In trying to understand this unusual effect, the reaction was carefully followed visually and it was noticed that, immediately after mixing, a very finely divided white-colored powder is formed, directly followed by the fast formation of bright white crystals, looking like a flash of lightning; the cracking is observed during this latter process.

The solid product has been analyzed by chemical analysis and IR and far-IR spectroscopy, and it was found that the compound is $ZnCl_2$pyr (pyr = pyrazine), identical with the compound prepared first by Stoehr.[1] However, the cracking was neither mentioned in this early report, nor in subsequent reports describing the spectroscopic properties and structure of this compound.[2] The IR and far-IR data of the final product are identical with those reported by other investigators.[3] From these data it has been concluded that the Zn(II) ion can be considered as hexacoordinated, with an octahedrally based geometry in which both halide and pyrazine are bridging between the metal ions.

On searching the literature, no other examples were found that show a similar effect, making an explanation of this phenomenon very difficult and presently only some effects that may be responsible for the cracking can be suggested.[4,6] A

Scheme II. Calculated π Charge Distribution and Dipole-Moment Components in Substituted Butadienes. The components μ^π have been calculated from the *point* π charges

Figure 1. Sound pressure level (S.P.L.) as a function of the frequency for one "crack" of the acoustic emission of crystallizing ZnCl₂Pyr.

possible explanation may be a phase transition in the crystal that damages the original crystal. Such a phase transition may be caused by a change in coordination geometry from initially formed, tetrahedrally coordinated Zn(II), with bridging pyrazines and terminal chloride ions, to octahedrally coordinated Zn(II), with both bridging pyrazines and chloride ions (the final product). A second possibility is the initial formation of relative short chains or dimers, followed by a rapid polymerization into infinite polymers. To investigate the nature of the acoustic emission, a frequency–intensity analysis has been performed. The sound pressure level (S.P.L.) of a single crack has been plotted as a function of the frequency in Figure 1. It is observed that the most intense sound emission is outside the region of the human hearing (which is up to ~16 kHz). The maximum in the S.P.L. curve at ~100 kHz is not accurately determined, owing to the use of a low-pass filter in the fast Fourier transform analysis. No measurements at all were possible above 160 kHz.

References and Notes

(1) Stoehr, C. *J. Prakt. Chem.*, **1895**, *51*, 449.
(2) Ferraro, J. R.; Wozniak, W.; Roch, G. *Ric. Sci.*, **1968**, *38*, 433.
(3) Ferraro, J. R. "Low Frequency Vibrations of Inorganic and Coordination Compounds", Plenum Press: New York, N.Y.; 1971.
(4) The authors are indebted to one of the referees pointing our attention to a paper[5] describing the crystalloluminiscence of Ba(ClO₃)₂ and of KNa₃(SO₄)₂. Acoustic signals registered by a hydrophone placed into the solution coincided with the luminescence.
(5) Belyaev, L. M.; Nabatov, V. V.; Martyshev, Y. N. *Soviet Phys. Crystallogr.*, **1963**, *7*, 464.
(6) A relationship with the well-known phenomenon of triboluminescence[7] was initially supposed. However, we were unable to detect any luminescence during or after the cracking.
(7) See, e.g., Zink, J. I. *Inorg. Chem.*, **1975**, *14*, 555; Hardy, G. E.; Baldwin, J. C.; Zink, J. I.; Kaska, W. C.; Liu, P. H.; Dubois, L. *J. Am. Chem. Soc.*, **1977**, *99*, 3552.

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Preparation and Crystal Structure of Oxotechnetium Bis(thiomercaptoacetate) and Its Relationship to Radiopharmaceuticals Labeled with 99mTc

Sir:

Because of the minute concentrations (typically 10^{-8} M) of technetium used in solutions of diagnostic imaging agents,[1-3] unambiguous identification of the chelated species present, or even of the oxidation state of the coordinated technetium, is difficult. Furthermore, the behavior[4,5] of technetium, partic-

Table I. Structural Parameters of {TcO[SCH₂C(O)S]₂}⁻

Distances, Å			
Tc–S₁	2.336 (3)	S₁–S₂¹	4.361 (4)
Tc–S₂	2.303 (3)	S₁–C₁	1.741 (12)
Tc–O₁	1.672 (8)	S₂–C₂	1.762 (13)
S₁–S₁¹	3.041 (5)	O₂–C₁	1.26 (2)
S₂–S₂¹	3.016 (6)	C₁–C₂	1.46 (2)
S₁–S₂	3.139 (4)		

Angles, degree			
S₁–Tc–S₁	81.2 (1)	Tc–S₁–C₁	106.5 (5)
S₁–Tc–S₂	85.1 (1)	Tc–S₂–C₂	105.9 (4)
S₁–Tc–S₂¹	140.1 (1)	S₁–C₁–O₂	117 (1)
S₁–Tc–O₁	109.7 (3)	S₁–C₁–C₂	118.9 (9)
S₂–Tc–S₂¹	81.8 (2)	O₂–C₁–C₂	124 (1)
S₂–Tc–O₁	110.2 (3)	S₂–C₂–C₁	115.6 (8)

ularly in the V and VI oxidation states, has not been extensively investigated. Prior to this study no technetium coordination complexes had been isolated from aqueous solution close to physiological pH (7.4).

We report the synthesis and crystal structure of a novel five-coordinate Tc(V) compound, (Bu₄N)[TcO(SCH₂COS)₂] (I).

The reaction of pertechnetate with thioglycolic acid (HSCH₂COOH) at pH 8.2 has been described as a colorimetric method for the quantitative determination of technetium.[6] In an attempt to isolate the technetium-containing species giving rise to the 655-nm absorption band described by Miller and Thomason,[6] complex I was obtained instead. Reagent thioglycolic acid (Fisher or MCB) was diluted to 10% v/v with distilled water and was adjusted to pH 7.5 with 50% w/w NaOH solution. Typically, 0.75 mL of 0.352 M NH₄TcO₄ solution (New England Nuclear) was added to 60 mL of the thioglycolate solution. After 10 min, 3 g of Bu₄NBr (Eastman) in 10 mL of distilled water was added, and a yellow-brown precipitate appeared. The precipitate was filtered, washed with water, and successively recrystallized from methanol–water and acetone–water mixtures.

The compound[7] crystallizes in the monoclinic space group C_m, confirmed by refinement.[8] The dimensions of the unit cell are $a = 10.451$ (5) Å, $b = 14.855$ (8) Å, $c = 9.927$ (7) Å, $\alpha = \gamma = 90°$, $\beta = 114.88$ (5)°, with two molecules per unit cell.

An Enraf–Nonius CAD4 diffractometer was used for the collection of intensity data on a crystal of dimensions $0.1 \times 0.3 \times 0.35$ mm, using a $\theta–2\theta$ scan employing graphite monochromatized Mo Kα radiation ($\lambda = 0.7103$ Å). The range of data collected was $0° < 2\theta$ (Mo Kα) $< 60°$. A total of 2207 independent reflections was collected.

Lorentz and polarization corrections were applied to the data, and an absorption correction was made using an empirical ψ scan correction.[9]

The structure was solved using the Patterson method. The Patterson map showed the position of the technetium atom, and the remaining nonhydrogen atoms were located in succeeding difference Fourier syntheses.

Only the 1248 reflections having $F_{OBS}^2 > 3\sigma(F_{OBS}^2)$ were used in the least-squares refinement, which resulted in final values of $R_1 = 0.082$ and $R_2 = 0.091$. The final difference Fourier map showed no residual electron density as high as 0.5 carbon atom on a previous difference Fourier map.

The anion was found to lie on a crystallographic mirror plane. The *n*-butylammonium cation was also found on the mirror plane and determined to be 50–50 disordered in all *n*-butyl chains. Anion bond lengths and bond angles are presented in Table I.

The technetium atom (Figure 1) is coordinated by an oxygen and four sulfur atoms in very nearly a square pyramid, with the sulfur atoms forming the basal plane and the oxygen atom