L_3-Edge Anomalous Scattering of X-rays by Praseodymium and Samarium

Sir:

We report measurements of the anomalous scattering of X-rays by atoms of praseodymium and samarium at wavelengths through their L_3 absorption edges. Values of both f' and f'', the real and imaginary components of the anomalous scattering, were derived from diffraction experiments using synchrotron radiation. Both components exhibit exceptionally large changes in a narrow interval of wavelength, changes which offer a powerful tool for solving the phase problem in crystal structure analysis.

Synchrotron radiation provides a continuous X-ray spectrum intense enough for single-crystal diffraction experiments at arbitrary wavelengths selected by a narrow-band-pass crystal monochromator. Experiments with cesium hydrogen tartrate[1,2] showed that f' for cesium dips to -26.7 ± 0.3 electrons and f'' rises to 16.1 ± 0.8 electrons near the L_3 edge (2.474 Å). These effects are large enough to be useful in solving macromolecular crystal structures, but cesium is not very convenient for this purpose because of strong absorption of X-rays by light atoms at this wavelength. The rare earth elements have L_3 edges (2.26 Å for lanthanum to 1.34 Å for lutetium) which span the wavelength range normally used to study large molecules. X-ray absorption spectra[3] for several rare earth compounds show sharp and intense lines at the respective L_3 edges, indicating anomalous scattering effects as large or larger than those for cesium. This indication is confirmed by the present results.

The method[4] is to use least-squares adjustment to derive f', f'', and a scale factor from diffraction intensities measured at the wavelength of interest with a crystal whose structure is known from a conventional experiment at another wavelength. We used crystals of sodium praseodymium ethylenediaminetetraacetate octahydrate ($NaPrC_{10}H_{12}N_2O_8{\cdot}8H_2O$) and the isomorphous samarium salt which, like the same salts of most of the other rare earth elements, crystallize in the noncentric space group *Fdd*2.[5-7] The atomic coordinates and thermal parameters were determined using Mo Kα radiation.[8] In one praseodymium experiment we measured 970 reflections (without any repetitions) in the range $0.08 < \lambda^{-1} \sin\theta < 0.42$. At each other wavelength we measured 48 reflections in the range of $\sin\theta/\lambda$ from 0.37 to 0.41, including 23 Bijvoet pairs and two centric reflections, from one to three times each. One reflection was repeated after each 10 or 12 measurements to serve as an intensity standard. Subsequent studies of the standard-reflection profiles indicate changes in wavelength during some of the praseodymium experiments, probably caused by movement of the monochromator mechanical support. Corrections as large as 0.0011 Å based on the observed changes in Bragg angle are included in the wavelengths listed in Table I. Absorption corrections were calculated by analytical integration[9] with the crystal shapes described by 9 or 10 plane faces and absorption coefficients ranging from 100 to 460 cm^{-1}. Other details of the method and apparatus are described elsewhere.[1,2,10,11]

The values found for the anomalous scattering terms are plotted in Figure 1 and listed, with the respective *R* values for each data set, in Tables I and II. For both elements, f'' exhibits the striking resonance line which is observed in the absorption curves. The peak values are substantially larger than we observed for cesium, and in the praseodymium case more than double the values for any element near K or L edges calculated by Cromer and Liberman[12] with a model which neglects fine structure lines.

Table I. Praseodymium Anomalous Scattering

λ, Å	f'	f''	R^a
2.0833	−18.5 (6)	4.3 (6)	0.045
2.0817	−21.6 (5)	5.1 (4)	0.050
2.0810	−22.8 (5)	5.4 (4)	0.056
2.0805	−25.0 (7)	7.9 (6)	0.083
2.0796	−25.7 (6)	8.1 (4)	0.068
2.0790	−27.0 (2)	19.7 (2)	0.071[b]
2.0788	−25.8 (11)	22.3 (9)	0.056
2.0784	−24.0 (13)	25.6 (11)	0.053
2.0776	−16.7 (12)	27.3 (11)	0.035
2.0772	−14.8 (12)	26.9 (11)	0.038
2.0767	−6.6 (10)	18.7 (13)	0.036
2.0745	−10.3 (7)	10.5 (9)	0.036

[a] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [b] 970 reflections.

Table II. Samarium Anomalous Scattering

λ, Å	f'	f''	R
1.8512	−15.6 (5)	4.1 (6)	0.035
1.8490	−17.2 (5)	4.5 (5)	0.037
1.8479	−18.6 (5)	6.5 (5)	0.057
1.8468	−21.3 (10)	7.7 (10)	0.082
1.8463	−19.5 (10)	14.0 (13)	0.072
1.8457	−18.6 (8)	22.0 (7)	0.033
1.8452	−8.5 (16)	23.3 (18)	0.050
1.8441	−6.3 (18)	14.0 (24)	0.078
1.8425	−10.0 (9)	9.9 (12)	0.047
1.8397	−12.7 (10)	10.7 (12)	0.042

The curves for f' show the characteristic shape demanded by the dispersion relation for a sharp absorption line. In Figure 1 the broken lines show f' calculated from f'' by a Kramers–Kronig integration;[2] for this purpose the experimental f'' curve was extended to higher and lower wavelengths by estimated values. Errors in these estimates affect the calculated curve by an additive constant, but contribute little to its shape in this narrow wavelength interval. The agreement of the curves is excellent.

The wavelength spread of the X-ray beam from the monochromator, estimated as $\Delta\lambda/\lambda = 10^{-3}$, is comparable with the widths observed for the peaks in f' and f''. Thus it may be that even larger variations can be observed with more nearly monochromatic X-rays. We intend to test this possibility.

The use of f'' to help solve the phase problem in X-ray crystallography, by means of the intensity difference it causes for reflections *hkl* and $\overline{hkl}$, is well established. Larger values of f'' make the method more powerful. The effect of a change in f' is similar to that of a change in atomic number. Thus, experiments at two or more wavelengths where f' is different can be analyzed in the same manner as isomorphous replacement data. Again the utility of the method is sensitive to the magnitude of the changes in f'. Large anomalous scattering terms also facilitate the determination of heavy-atom positions. Once the positions are known for the anomalously scattering atoms, one can derive phase angles without ambiguity from diffraction data measured for one crystal at three or more wavelengths, or at two or more wavelengths if both members of each Bijvoet pair are measured. The phase angles are found by solving vector equations in the complex plane, for example as described by Singh and Ramaseshan.[13] If these equations are represented by a Harker diagram,[14] the centers of intersecting circles must be well separated and noncollinear for accuracy and uniqueness. These conditions are met if f'' is large enough for at least one wavelength and f' changes enough between two wavelengths. Hoppe and Jakubowski[15] showed that phases could be determined with an accuracy of ~50° for many of the reflections of a protein (erythrocruorin, mol wt ~16 000) using two wavelengths near the K edge of iron, where the anomalous scattering effects are about seven times smaller than those reported here for praseodymium. An atom of

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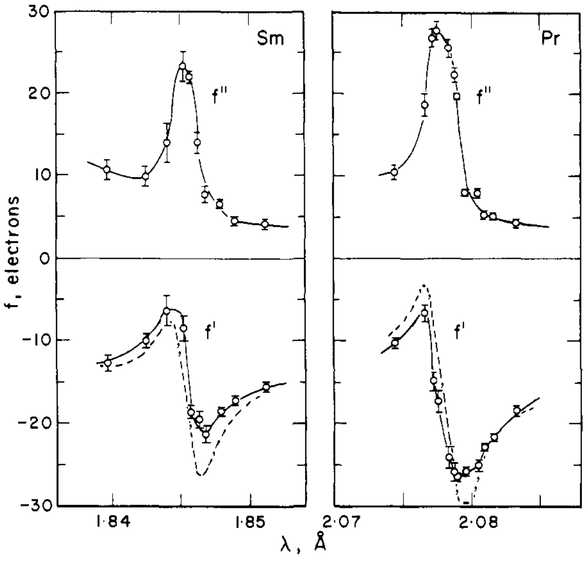

Figure 1. Anomalous scattering terms f' and f'' near the L_3 edges for samarium (left) and praseodymium (right). The broken lines are calculated from f'' by a dispersion relation.

praseodymium in a molecule of 800 000 daltons would be a somewhat similar case, since, according to Wilson statistics, the percentage effects of anomalous scattering depend on the ratio of changes in f to the square root of the number of atoms.[16]

Acknowledgment. The crystals for this experiment were prepared by Helena W. Ruben. We thank her and Dr. Allan Zalkin for cooperation in the determination of the structural parameters needed for this work, Dr. James C. Phillips and Professor Keith O. Hodgson for development of the diffractometer facility and its mode of operation at SSRL and for many stimulating discussions, and the staff members of SSRL, too numerous to list here, who helped make it possible for us to work with synchrotron radiation. This work was supported in part by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. W-7405-Eng-48. Some of the materials incorporated in this work were developed at the Stanford Synchrotron Radiation Laboratory which is supported by the National Science Foundation (under contract DMR77-27489), in cooperation with SLAC and the Department of Energy.

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Lieselotte K. Templeton, David H. Templeton*
Materials and Molecular Research Division
Lawrence Berkeley Laboratory and Department of Chemistry
University of California, Berkeley, California 94720

R. Paul Phizackerley
Stanford Synchrotron Radiation Laboratory and
Department of Structural Biology, Stanford University
Stanford, California 94305

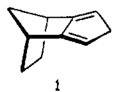
Received October 2, 1979

Electronic Control of Stereoselectivity. 3. Stereoselection Operative in [4 + 2]π Cycloadditions to Cyclopentadiene Rings Fused at C_2,C_3 to Bicyclic Frameworks[1]

Sir:

Exo addition to norbornene double bonds in the absence of sterically interfering C_7 substituents is so commonplace that transformations based upon this stereoselection have played a pivotal role in organic synthesis. Although exo attack has frequently been attributed to dominant steric control, the possible contribution of electronic factors has recently been addressed.[2,3] Using second-order perturbation theory, Fukui concluded that the higher energy of the norbornene π orbital leads to σ–π mixing in bonding fashion with all lower lying orbitals, the result giving rise to somewhat greater π-electron density in the exo region.[2] Houk's contrasting view is based upon an antibonding interaction between the $C_1C_6C_5C_4$ bridge and the π orbital, with resultant repulsion of electrophiles approaching the endo surface because of destabilizing secondary orbital interactions.[3]

Unambiguous demonstration of the existence of a directed electronic effect (exo) in norbornyl systems has long been awaited. Complications arise because of present inabilities to dissect steric factors which dictate exo stereoselection as well. We have reasoned that the orbital interactions existent in bridged bicyclic systems should have a recognizable impact at more remote sites which are not sterically biased.[4] The present study, which centers about the stereochemistry of Diels–Alder additions to **1**–**3**, provides evidence sufficient to justify consideration of norbornyl and norbornenyl frameworks as respectable electronic perturbers and constitutes amplification of earlier observations made by the research groups of Alder and Sugimoto.[5] Specifically, the examples presented herein suggest that electronic rather than steric factors govern the highly stereoselective approach of dienophiles to **1** and **2**. These factors are diminished in **3** which shows lower stereoselectivity in reactions with dienophiles.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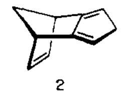
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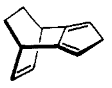
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Heating carbon tetrachloride solutions of **1** (42 °C, 10 h) and **2** (42 °C, 48 h) with methyl acrylate in sealed tubes afforded adducts **4** and **5**, respectively, as exclusive products in purified yields of 94 and 88%. Proof of the dienophile approach to the endo faces of **1** and **2** was gained by conversion of **5** into **4** and subsequent diimide reduction to give **7a** (Scheme I). Delivery of hydrogen to the norbornene-type double bond materialized expectedly from the exo direction as shown by conversion of **7a** into the thallium carboxylate **7b**, treatment

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