pressor component of sodium chloride, and that chloride merely permits the kidney to reabsorb more sodium than it otherwise would, Liebman and Langford do not appear to allow for the possibility that dietary chloride might induce hypertension through a mechanism other than the renal retention of sodium. It is of course possible that the anion of a dietary sodium salt could affect blood pressure by affecting only the renal reabsorption of sodium. However, in rats given DOC and in Dahl salt-sensitive rats, the finding that dietary sodium chloride induces hypertension, but equimolar amounts of nonchloride containing sodium salts do not, could not be related to more positive external balances of sodium or to greater weight gain in the rats given sodium chloride (*2–5*). These observations do not support the notion that anions other than chloride block the blood pressure-raising effects of sodium simply by decreasing tubular reabsorption of sodium. The fact that provision of supplemental potassium chloride can attenuate the severity of hypertension does not exclude the possibility that some effect of chloride contributes to sodium chloride–induced hypertension.

Liebman and Langford state that it may be difficult to reproduce the finding that the anionic component of the sodium salt consumed can be a determinant of blood pressure. This finding, however, has been consistently observed in studies of the DOC model of hypertension in three separate laboratories (*2, 3, 5, 6*). The phenomenon occurs in the absence of impairment of weight gain (*2, 3, 5*).

Studies conducted thus far suggest that all sodium salts do not have the same potential to induce increases in blood pressure (*2–8*). If dietary sodium salts were shown to vary widely in their hypertensinogenic capacities in the human, the finding would have considerable relevance to the pathogenesis of "sodium-dependent" hypertension.

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Electron Density Distribution in the Organic Superconductor $\mathrm{(TMTSF)_2AsF_6}$: Fact and Fancy

In a recent report, Wudl *et al.* (*1*) claim to have obtained experimental evidence from x-ray analysis for bonding electron density between selenium atoms belonging to different molecules of tetramethyltetraselenafulvalene (TMTSF) in the organic metal $\mathrm{(TMTSF)_2AsF_6}$. The crystal structure is built from stacks of TMTSF molecules and sheets of $\mathrm{AsF_6}$ anions. The evidence for bonding density consists of various features seen in an electron-density difference map. Peaks occurring between molecules of the same TMTSF stack are considered to be "a microscopic view of electron density distribution along a one-dimensional conduction band," whereas peaks between selenium atoms belonging to different stacks show that "there is a continuum of density from one molecule to the other that may represent a conduction band" (*1*, p. 417). Apart from the question why peaks in the difference map (regions of excess electron density) should be considered to represent a conduction band associated with removal of electrons from the neutral TMTSF molecules, the claims put forward in the *Science* report (*1*) are so remarkable that they can hardly avoid drawing specially critical attention to the evidence on which they are based.

A careful evaluation of the evidence seems all the more necessary because the high proportion of heavy elements in the crystal implies that bonding effects will be very small compared with the sum of the core densities and hence very difficult to detect experimentally. Indeed, the suitability factor of the compound $\mathrm{(TMTSF)_2AsF_6}$ for a charge-density study, as defined by Stevens and Coppens (*2*), is only 0.11, compared with about 3 to 4 for a light-atom structure. A value as low as 0.11 requires extreme accuracy in the x-ray measurements and in the parameters describing the promolecule (*3*), if the difference map is to mean anything at all (*4*).

Unfortunately, the full experimental details of the work have not yet been disclosed (*5*). Yet, from the limited information provided, there is no indication of any claims for extraordinary accuracy. In fact, the main conclusions are drawn from difference maps based on room-temperature data containing only (*1*, p. 416) "minimal high-angle scattering, presumably due to a 1/3–2/3 rotational disorder observed in the $\mathrm{AsF_6}$ groups." Although low-temperature (−113°C) measurements were also made, the resulting difference maps were considered to be inferior to those from the room-temperature study for reasons that appear to depend on the authors' a priori judgment about what the residual electron density ought to look like: "some common sense is required in the interpretation of what is an artifact of the experiment and what is 'real' electron density" (*1*, p. 417).

We are left with the internal evidence of the electron-density difference maps, which constitute figures 1 through 4 of the report (*1*). Of these, figure 1, showing the difference density in the plane of the TMTSF molecule, is the most revealing for an assessment of the quality of the maps. Although the site symmetry of the TMTSF molecule in the crystal is only C_1, its electron density can be expected to correspond closely to the D_{2h} molecular point group. In fact, density features corresponding to chemically equivalent parts of the molecule are of quite different shapes, sizes, and strengths; for example, one selenium atom is accompanied by a strong peak in the molecular plane, in the sp^2 lone-pair region, but the other three selenium atoms lack this feature. It is also apparent that all the atomic centers are in regions of strong negative density, pointing to a slight error in the scale factor. Since the integral of the difference density over the unit cell must vanish, this negative density must necessarily be compensated by positive density in other regions of the crystal. Thus, many features of the difference density in the molecular plane, where it can be checked to some extent, do not seem particularly meaningful and are almost certainly due to errors in the measurements and in the parameters. It therefore seems prudent to reserve judgment about the significance of features of the difference map in the other regions where no such checks are possible.

The importance of accurate charge-density maps for studying chemical bonding can hardly be denied, but at the same time the experimental difficulties involved in obtaining such maps, particularly for heavy-atom compounds, should not be underrated. The experimental uncertainties in the x-ray analysis reported by Wudl *et al.* are so great that very little confidence can be placed in the details of the difference maps. Of course, as in any distribution marked by a high noise level, there are peaks, troughs, ridges, and valleys, and there is a language of electron-density concepts only too ready to be projected onto them.

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3. For explanations of terms current in the jargon of charge density analysis, see P. Coppens, in *Electron Distributions and the Chemical Bond*, P. Coppens and M. B. Hall, Eds. (Plenum, New York, 1982), p. 61.
4. R. F. Ziolo and J. M. Troup [*J. Am. Chem. Soc.* **105**, 229 (1983)] recently claimed to have obtained significant evidence for donor-acceptor bonding density from difference maps of dimethyltellurium dichloride, with a suitability factor as low as 0.07. Although this claim has been given considerable prominence [for example, in *Chem. Eng. News* **61** (No. 5), 17 (1983)], the arguments and the evidence proffered are no more convincing than those in the *Science* report. In particular, there is no attempt to provide an objective assessment of the reliability of the results. It is not enough to find "complete agreement between our data and what we believed we'd see" (attributed to Troup in the *Chemical Engineering News* article), especially when this "complete agreement" in the difference maps was achieved by excluding medium- and high-order reflections ($\sin \theta/\lambda > 0.4$ Å^{-1}) from the calculation.
5. They are promised as part of a full account to be published elsewhere. The crystal-structure analysis of $(TMTSF)_2AsF_6$ has been described [F. Wudl, *J. Am. Chem. Soc.* **103**, 7064 (1981)].

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Comments on our report (*1*) by Dunitz (*2*) demand a reply. Dunitz's comments can be reduced to five specific statements:

1) Although conduction electrons would be "invisible" in an electron density determination experiment, regions of orbital overlap (essential for band formation) would be visible. What we meant in our report (*1*) was that the buildup of electron density between tetramethyltetraselenafulvalene (TMTSF) molecules is indicative of the orbital overlap necessary for band formation. As we pointed out (*1*), the features of our maps are in remarkable agreement with the results of Grant (*3*), particularly in view of the fact that neither Grant nor we were aware of each other's work while it was in progress.

2) The second paragraph of Dunitz (*2*) contains an allusion to the fact that the suitability factor for $(TMTSF)_2AsF_6$ is "only 0.11. . . . " The suitability factor as defined by Stevens and Coppens (*4*) was not proposed for use as a criterion for ruling out an electron density study. In fact, there is a study on the superconductor V_3Si in which the suitability factor was 0.05 (*5*).

3) We agree with Dunitz that high accuracy and the best possible data should be used for electron density studies. In our study extensive data sets were collected on ten crystals at high and low temperatures and the best refinement and electron density map were reported (*6*).

We do not feel that the "experimental uncertainties" are so great as to discredit our result. In the various refinements and electron density maps produced during this study, various chemically reasonable bonding and lone-pair electron density features were found to be common to all data sets and crystals. The reported electron density maps clearly showed these features. The internal consistency and the agreement of electron density with current bonding theory in our opinion is too good to be fortuitous. In this respect even Dunitz and Seiler (*7*) must allow flexibility in what is suitable for an electron density map as shown by their examination (*7*) of a material that decomposed upon exposure to x-rays. To generate maps, data sets of two different crystals with different degrees of decomposition and different data treatment were jointly used for the study; positional and thermal parameters were determined from one data set, and the electron density calculations were carried out with the use of a different set. It is apparent that "extreme accuracy" could not be achieved by the above treatment and apparently was not a limiting factor for the generation of electron density maps.

4) A statement regarding our rejection of the low-temperature map was made in paragraph 3 of Dunitz (*2*). We contend, and have observed, that electron density information is only enhanced (not created) relative to background at low temperature. In $(TMTSF)_2X$ ($X = AsF_6$, PF_6) at low temperature, large regions of electron density were observed around selenium atoms; these regions were not observed at room temperature. This was explained as the result of a solid-state phase transition at low temperature. The creation of this density at low temperature has to be due to factors other than true electron density, or some evidence of this density would have appeared at room temperature as well; hence, our statement (*1*) about "common sense."

5) Apparently our point about hybridization (*1*) was missed [see paragraph 4 of Dunitz (*2*)]; the unusual feature of the map in question is that sp^3 lobes of one selenium have extended more into the TMTSF plane than those of the remaining selenium atoms and not that one has density and the others do not. In our studies we have not restricted ourselves to the examination of molecular planes only but have looked for features in all other regions near the molecules in question (although the publication of all maps is not feasible). The implication that all the positive density features in the molecular plane are meaningless because of the negative density at the atomic centers is unwarranted. Although it is true that "negative density must necessarily be compensated by positive density in other regions of the crystal" (*2*, p. 353), this applies only to the summation of the density over the whole unit cell and there is no corresponding restriction to an individual plane. More importantly, the estimated errors in charge density are not uniform throughout a unit cell, as pointed out by Stevens and Coppens (*4*). Near the nuclear positions errors in the difference densities are relatively large and are dominated by uncertainties in the atomic parameters and the scale factor, whereas away from the nuclear positions experimental errors in observed densities dominate. Coppens has noted that, even when a relatively heavy atom is present, acceptable errors away from the atomic positions are achievable (*8*).

Qualitatively, all expected bonding and lone-pair densities are present and those intermolecular electron densities that were calculated to be absent are absent in the reported study (*1*). It seems unlikely that this consistency is accidental. Therefore, if we believe the intramolecular features for which we know the answers are qualitatively correct, we must also believe similar, intermolecular features.

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