Constitution of Calycanine

SOME time ago, on the suggestion of Prof. A. R. Todd, calycanine was examined by X-ray methods[1,2] in order to decide whether a constitution originally suggested by Barger, Madinaveitia and Streuli[3] for a molecule $C_{16}H_{10}N_2$ is in harmony with the crystallographic symmetry and the unit cell dimensions. That investigation established the approximate dimensions of a monoclinic unit cell as $a = 13{\cdot}7$ A., $b = 4{\cdot}45$ A., $c = 9{\cdot}7$ A., $\beta = 107°$, and showed that the space group is $P2_{1/a} - C_{2h}^5$, provided that a few very weak reflexions are neglected. If these reflexions are taken into account, it was suggested that the above cell should be regarded as a pseudo-cell, the true unit cell having a doubled c-axis, $2 \times 9{\cdot}7$ A. Fairly detailed suggestions were advanced as to the probable crystal structure, but the chemical synthesis which Prof. A. R. Todd intended to carry out has not been completed because of the War.

Recently, Prof. Todd pointed out to us that a totally different molecule $C_{21}H_{15}N_3$ has been proposed by Manske and Marion[4], and suggested that our X-ray data might enable us to decide unequivocally whether this new molecule can be regarded as a possible alternative to the molecule $C_{16}H_{10}N_2$. We have therefore re-examined our original X-ray data, and have supplemented it with new photographs from different crystalline specimens, with the following results.

The dimensions of the monoclinic (pseudo) cell have been determined more accurately as $a = 13{\cdot}7$ A., $b = 4{\cdot}45$ A., $c = 9{\cdot}8$ A., $\beta = 110{\cdot}5°$. The density of calycanine is 1·34 gm./c.c., so that the mass of this unit cell is 750×10^{-24} gm. The masses of molecules $C_{16}H_{10}N_2$ and $C_{21}H_{15}N_3$ are 379×10^{-24} gm. and 510×10^{-24} gm., so that this cell would contain $\frac{750}{379}$ or $\frac{750}{510}$ molecules, that is, 1·98 or 1·47 molecules, according as one formula or the other is selected. Thus within the accuracy of our measurements this cell may contain either two molecules $C_{16}H_{10}N_2$ or $1\frac{1}{2}$ molecules $C_{21}H_{15}N_3$. If this is the true unit cell, the second alternative can be rejected, since a unit cell cannot accommodate a fractional number of molecules.

In general, an approximate determination of the cell dimensions and density would suffice to decide between alternative molecular formulæ; in this case, however, it happens that a cell with doubled c-axis (as suggested in our original examination of calycanine[1,2]) would contain a whole number of molecules (four or three) for either of the molecules proposed. It therefore becomes necessary to consider very carefully the significance to be attached to the additional weak reflexions which originally led us to propose a true unit cell with doubled c-axis.

Our new photographs again show additional weak reflexions, but, partly because of the shape of these diffraction spots, partly because of their positions in the oscillation photographs, and partly because of the difficulty we have found in systematizing their appearance in photographs from different crystalline specimens, we now incline strongly to the view that they arise from one or more differently oriented crystalline fragments attached to, or grown as part of, the main crystal exposed to the X-ray beam. Because of the peculiar optical properties of calycanine[1], such crystalline fragments are not detected by the usual microscopic examination. The possibility of a true unit cell with doubled c-axis is not definitely excluded; but we do not now consider that there is any very definite evidence for its existence, and if the *true* unit cell has $c = 9{\cdot}8$ A., then the formula $C_{21}H_{15}N_3$, suggested by Manske and Marion, is apparently excluded, while the formula $C_{16}H_{10}N_2$ suggested by Barger, Madinaveitia and Streuli and by Prof. Todd is acceptable. The detailed discussion[1,2] of the probable crystal structure is unchanged in essentials, though slightly modified in detail, if the small cell ($c = 9{\cdot}8$ A.) is the true unit cell.

If, however, we still take the cautious view that the true cell may have the doubled c-axis, it is still necessary to consider under what conditions three molecules ($C_{21}H_{15}N_3$) could be accommodated in it. It appears that this would necessitate the selection of *either* a triclinic space-group *or* a monoclinic space-group without $\{h0l\}$ halvings, so that in either case well-established features of the crystal symmetry must be left out of account. No such difficulties arise, of course, in placing four molecules ($C_{16}H_{10}N_2$) in the larger cell.

We may summarize by saying that all the evidence, whether direct or circumstantial, is satisfactorily explained if the molecule is $C_{16}H_{10}N_2$; but that a molecule $C_{21}H_{15}N_3$ can only be brought into harmony with observation by the adoption of a series of unusual and unlikely suppositions which still leave unexplained certain prominent features of the experimental data.

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[1] Hargreaves, A., thesis for Ph.D. degree, University of Manchester (1940).
[2] Hargreaves, A., and Taylor, W. H., *J. Sci. Instr.*, **18**, 138 (1941).
[3] Barger, G., Madinaveitia, J., and Streuli, P., *J. Chem. Soc.*, 510 (1939).
[4] Manske, R. H. F., and Marion, L., see Craig, *Ann. Rev. Biochem.*, **11**, 572 (1942).

Non-Solar Planetary Systems

OBSERVATION has revealed the existence of at least two planetary systems attached to binary stars very near our solar system[1]; and the suggestion that there are numerous planetary systems in the universe gains ground. It is interesting to examine the different conflicting theories of the origin of the solar system in the light of these observations.

On the tidal theory of Jeans and of Jeffreys, planetary systems originate only at the rate of about one per 5,000 million years. Taking the generally accepted short time-scale for the age of the universe —an interval between 10^9 and 10^{10} years—we find that there can be at most two planetary systems in the galactic system, on Jeans's theory. The probability of collisions is still less on Lyttleton's binary star collision theory[2], and there is scarcely any chance for the formation of a planetary system.

On Banerji's Cepheid theory[3], in which the solar system is supposed to originate from the oscillatory instability of a Cepheid due to the gravitational attraction of a passing star, the probability of formation is very much greater, as a grazing or even close encounter is not necessary in this theory. In fact, Banerji concludes his theory with the following words: "One conclusion seems to be irresistible. If the theory be correct in its essentials, there may be more planet-