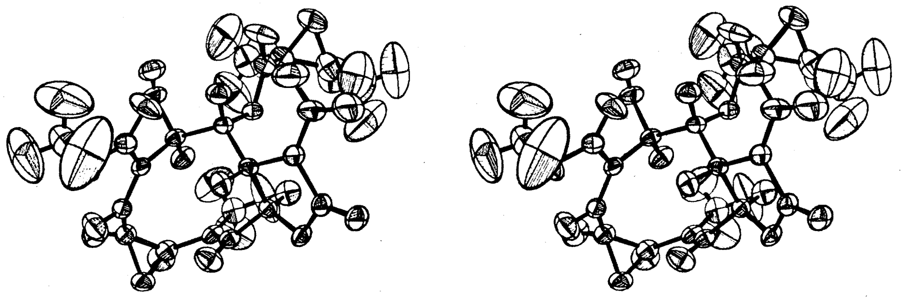

Fig. 2. Stereopair diagram of melampodin.

unit cell parameters are $a = 8.990$, $b = 14.352$, and $c = 16.294$ Å; the number of molecules in the unit cell, Z, is 4; the space group is $P2_12_12_1$; Q_H is 21.9 percent; and the wavelength of incident neutrons is 1.0142 Å. A total of 2884 independent reflections were measured and converted to normalized structure factors (E's). Of these, 414 were in the range 1.40 to 3.21 and were used to generate 2000 Σ_2 relationships. The computer program MULTAN *(6)* automatically selected three reflections (11,0,3; 4,0,3; 0,3,1) for origin definition, and assigned a phase of 90° to each. Another reflection (3,2,1) was assigned, in turn, the phases 45°, 135°, 225°, and 315°, while the reflection which fixed the enantiomorph (6,8,4) was assigned alternately the phases +45° and −45°. These eight combinations were used as starting phases in the tangent formula *(7)* as implemented by Germain *et al.* *(6)* to produce eight sets of refined phases for all 414 reflections. These eight sets actually represent only four unique possible solutions, since the sets are equivalent in pairs and differ only in the enantiomorph assignment. The associated figures of merit (*6*) range from 1.86 to 1.39.

The only E-map computed was that with the set of phases having the highest figure of merit and the angle $\alpha(6,8,4)$ equal to +45°. A model of the 22 largest maxima on the E-map showed all 13 of the skeletal atoms in the two fused rings (Figs. 1 and 2), three peripheral atoms, and only four spurious peaks. In all, 16 of the 21 carbon atoms and 5 of the 9 oxygen atoms were located directly from the E-map. Subsequent comparison with the atomic positions found in the x-ray analysis (*8*) revealed that the x-ray and neutron solutions differed only in the assignment of the enantiomorph. Since our experiment is not sensitive to the absolute configuration, we reversed the sign of the phase of the 6,8,4 reflection to conform to the x-ray assignment.

A standard analysis of the 2303 observed intensities produced a refined model of melampodin, all 54 atoms of which were allowed to vibrate anisotropically, with an agreement index, R, of 0.050; a weighted agreement index, R_w, of 0.041; and an error of fit of 1.082.

We must conclude that Sikka's upper limit of 100 atoms per unit cell for direct solution of neutron data is far too conservative. Under the conditions of our experiment (availability of good crystalline material, a complete set of high-quality data, and a relatively large contribution from "randomly" located positive scatters) it should be possible to solve nearly any neutron diffraction structure without recourse to x-ray diffraction results. Indeed, we have shown that neutron diffraction may be used as a primary tool in the structural investigation of moderately complex molecules, a fact which is of particular importance when hydrogen plays a prominent role in stereochemistry. Examples of interest to molecular biologists include hydrogen bonding, bond torsion angles in strained rings, hindered rotations, zwitterion structure, and protonation and hydrogenation products. These structural problems can be accurately elucidated only by neutron diffraction, since neither the atomic positions nor the thermal motion of hydrogen atoms can be detected with sufficient accuracy by means of x-ray analysis.

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A New Newton's Law of Cooling?

Abstract. *Several physiologists confuse Fourier's law of animal heat flow with Newton's law of cooling. A critique of this error in 1932 remained ineffective. In 1969 Molnar tested Newton's cooling law. In 1971 Strunk found Newtonian cooling unrealistic for animals. Unfortunately, he called the Fourier formulation of animal heat flow, requiring post-Newtonian observations, a "contemporary Newtonian law of cooling."*

A warm body without internal heating surrounded by a cold environment loses temperature faster, the greater the difference between the body temperature T_b and the ambient temperature T_a. This is Newton's law of cooling, published in the year 1701 (*1*). It can be formulated as follows:

$$dT_b/dt = k_N(T_b - T_a) \qquad (1)$$

where k_N is Newton's cooling constant.

Molnar (*2*) reproduced Newton's thermometer with linseed oil as the expanding liquid. He used this thermometer itself as the cooling body in order to investigate the conditions under which the temperature loss by cooling, ΔT_b, follows the logarithmic form of Newton's law of cooling:

$$\ln(T_b - T_a)_t = \ln(T_b - T_a)_0 - k_N t \qquad (2)$$

where 0 is the start of the measurement and t is the time from start.

An instrument for measuring the cooling effect of a cold environment on a warm body is called a katathermometer (*3*). The simplest form of it is a true Newtonian coolometer. Count Rumford called it a "passage thermometer" and, covering it with a layer of cloth, used it to determine the insulating power of material for uniforms (*4*).

When in observations of sufficient duration on homeothermic animals the small effects of cyclic deviations of the body temperature from homeothermy (for example, circadian changes of body temperature) are canceled, then Newton's cooling law loses its application because in truly homeothermic animals there is no cooling (*5*). Molnar (*2*, p. 9) states explicitly that "by cooling we mean only the fall in temperature not the transfer of heat." When Newton, in describing his observations on cooling which led to his law, used the term "heat," he meant what we now call "temperature." This was made clear by Mach (*6*).

The evolution of the modern concept of heat has required a century of temperature measurements in mixing trials after Newton's time. The result of this evolution enabled Black to teach his caloric theory, which clarified the relation of heat and temperature (*7*). A part of Black's caloric theory, namely the hypothesis that heat is a material substance, was later shown to be an error. According to Tyndall (*8*) Count Rumford "annihilated" the material theory of heat (*4*). Rumford proved (i) that heat, unlike any proper material substance, is weightless and (ii) that heat can be produced by work against friction in unlimited amounts, unlike water, which can be squeezed out of a sponge only as long as the sponge is wet. Heat resembles sound, which can be produced without limit by striking a bell.

The material part of the caloric theory is dead; calories are no longer conceived as molecules of a heat substance. But, like the mythical bird phoenix, the caloric theory has risen from the ashes to a higher level of existence; calories are now recognized as abstract quanta of a form of energy known as heat. We no longer believe that heat is a material substance, yet we speak of heat flow as if heat were a liquid. This is a very useful fiction applied in our calculations of heat transfer.

When Fourier (*9*) formulated his law of heat flow in 1822, he may have shared the material theory of heat with the majority of contemporary physicists because at that time Count Rumford's rejection of a material "caloric" was not yet generally accepted, as the story of Mayer's discovery of the law of conservation of energy shows (*3*). But Fourier's law of heat flow was correct even when formulated in the belief that heat is material; it is also correct now when it is known that heat is a form of energy. The difference between Fourier's law of heat flow and Newton's law of temperature loss is clear in the publications of physicists, for example, in Mach's book (*6*) or in that of Worthing and Halliday (*10*). Among physiologists, however, the two laws are still confused, as were the concepts of heat and temperature in Newton's time.

In 1932 Kleiber (*5*) applied an especially simple form of Fourier's law to the heat flow in the body of homeothermic animals schematized as a core with a constant temperature T_b surrounded by an insulating layer with heat conductivity λ, thickness L, surface area S, and surface temperature T_s. For these conditions Fourier's law of the rate of heat flow, dQ/dt, may be written as follows:

$$\frac{dQ}{dt} = \lambda \frac{S}{L}(T_b - T_s) \qquad (3)$$

Most physiologists specializing in homeotherms regarded the relation between the rate of heat flow and the difference in temperature between body and environment as being expressed by Newton's law of cooling. Richet wrote in 1889 (*11*), "conformément à la loi de Newton, un animal dégage d'autant plus de chaleur que sa température dépasse davantage le milieu ambiant" ("according to the law of Newton an animal gives off more heat the more its temperature exceeds the ambient temperature").

Harris and Benedict (*12*) criticized the application of Newton's law as a basis for the surface law of metabolic rate. They wrote, "physiologists have stated the physical law as they would like it to be rather than as it really is."

Hardy (*13*) stated that radiation conduction and convection can usually be lumped together as cooling or heating in accordance with Newton's law. His equations, however, express heat exchange, not Newton's temperature loss. Burton and Edholm (*14*) expressed clearly Newton's law of cooling as the exponential fall of the temperature of a warm body in time, but on the same page they also called the linear time relation between heat flow and temperature difference Newton's law of cooling. This error was repeated by Henshaw (*15*).

Equation 3, formulated in 1932, may have been the first explicit application of Fourier's law of heat flow to the heat transfer of homeothermic animals, as architects and engineers apply this law to estimate the thermostatic heat requirements of houses. Physiological publications dealing with Fourier's law remained rather rare. Barnett and Mount (*16*) stated that, in practice, the difference between the law of Fourier and that of Newton is not great. This remark shows a misunderstanding. The difference between the two laws is qualitative; it is as great as the difference between temperature and heat. "The two laws describe two different processes, and one must use the correct law for each process."

The last statement is quoted from an article by Strunk (*17*), who discussed the possibility of basing a new Newton's law of heat flow on Newton's old law of cooling. The author reached the result expressed in the first sentence of his abstract (*17*, p. 35), "The conditions necessary for true Newtonian cooling to occur are unrealistic for an animal." The abstract contains the explanation that the discussion is within the framework of Fourier's law. Strunk also stated that (*17*, p. 38) "all further reference to Newton's law of cooling will mean equation 7 and not Newton's original proportionality"; in his article equation 7 follows equation 6, which shows that for a body with a particular heat capacity the rate of heat flow is proportional to the rate of temperature loss.

The "Newtonian animal" is a model showing the conditions for applying Newton's "contemporary law of heat loss" (*17*, p. 37). It is a body with a material of sufficiently high heat conductivity that the difference between the temperature at the center and that at the surface is negligible in comparison with the temperature drop from surface to ambient temperature. An example of a Newtonian animal is a metal cast of the skinned carcass of a mouse to which the skin is stitched. A paradoxical increase in resistance to heat flow when the skinned carcass is replaced with a metal cast was explained by a decrease of the conductivity of the skin due to drying during removal from the carcass and stitching to the metal cast (*18*). A live mouse would be a more realistic model for animal heat flow. Its temperature regulation with blood circulation provides a core of uniform temperature surrounded by an insulating surface layer.

This is a model based on Fourier's law of heat flow. The linear relation between the rate of heat flow at constant core temperature and the temperature difference between core and surface is what most physiologists, especially those dealing with homeotherms, have in mind when they write of Newton's law of cooling, thereby confusing cooling with heat flow and Newton with Fourier.

Strunk's critical analysis of the application of Newton's law of cooling to animal heat flow is a very valuable supporting addition to earlier critiques of erroneous statements involving this law. However, the use of "contemporary Newton's law" for a formulation that cannot be Newtonian, and of "Newtonian animal" for a system without internal heat production, which contradicts one of the most basic criteria of an animal, may become a source of confusion.

For the sake of semantic clarity and historical truth it would be much better to admit that a number of first-rate physiologists, biophysicists, and zoologists have erroneously called Fourier's law of heat flow Newton's law of cooling. This mistake should be recognized and, in future publications, avoided. A simple form of Fourier's linear law of heat flow in animals without loss of body temperature (homeotherms) should be clearly distinguished from Newton's exponential law of temperature loss of a cooling body. The "heat conductivity" of the insulating layer in Fourier's law may be expanded to "heat transferability," and likewise "conductance" to its reciprocal, "resistance to heat flow." This extension makes Fourier's law of heat flow similar to Ohm's law of the flow of electrons.

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Crystal Structure of Krypton Difluoride at −80°C

Abstract. *Krypton difluoride is tetragonal, space group* P4_2/mnm, *with two linear molecules per unit cell aligned in planes perpendicular to the tetrad axes. The alignment alternates by 90 degrees between successive planes. The krypton-fluorine bond distance is 1.89 ± 0.02 angstroms.*

Crystals of KrF_2 at room temperature were studied by x-ray diffraction by Siegel and Gebert (*1*) with limited results. They reported a tetragonal lattice with unit cell parameters $a = 6.533$ Å and $c = 5.831$ Å, but were not able to identify the space group symmetry. Since KrF_2 is the only fully established binary compound of Kr it is important to know its crystal structure. We here report the KrF_2 structure as determined from low-temperature x-ray diffraction techniques.

Krypton difluoride was prepared by the method of Schreiner *et al.* (*2*). The material was distilled into a fluorinated ethylene propylene copolymer capillary (30 cm long, 1 mm outer diameter) and crystallized in a cold gas stream. A section 2 cm long containing a crystal was sealed off by keeping the section under liquid nitrogen while using the sealing torch above the liquid nitrogen surface. The specimen was stored in liquid nitrogen until it was placed in a cold gas stream on the x-ray apparatus.

The initial crystal was sublimed and recrystallized several times in a variety of crystallographic orientations relative to the capillary axis. Diffraction data were recorded at about −80°C by using a precession camera. The crystal symmetry was confirmed as tetragonal from Polaroid photographs of six zero levels and one upper level of the reciprocal lattice with a [100] orientation along the spindle axis (*3*). The unique reflections of observable intensity were 10 *hk*0, 14 0*kl*, 2 *hhl*, and 18 *hkl* reflections. The space group extinctions are 0*kl* absent unless $k + l = 2h$. The possible space groups are $P4_2/mnm$, $P\bar{4}n2$, and $P4_2nm$. The unit cell constants are

$$a = 4.585\ \text{Å} \qquad V = 122.5\ \text{Å}^3$$
$$c = 5.827\ \text{Å} \qquad Z = 2$$
$$\text{density} = 3.301\ \text{g cm}^{-3}$$

where V is the volume and Z the number of formula units in the unit cell. The a axis reported by Siegel and Gebert (*1*) is $2^{1/2}$ times longer than the true axis.

Visually estimated intensities of 20 reflections were obtained from the *hll* level of a crystal with a [011] orientation (*4*) and approximate dimensions of 0.2 by 0.1 by 0.1 mm. The data were corrected for the Lorentz and polarization effects but not for absorption. The structure was solved by placing Kr at 0,0,0 and F at $x,x,0$ in space group $P4_2/mnm$ (*5*) with $x = 0.2902$. The trial parameter was obtained by assuming

$$d_{\text{Kr-F}} = d_{\text{Xe-F}}(V_{\text{KrF}_2}/V_{\text{XeF}_2}) = 1.882\ \text{Å}$$

where $d_{\text{Xe-F}} = 2.00$ Å is the bond distance and $V_{\text{XeF}_2} = 130.15$ Å^3 is the unit cell volume as reported by Levy and Agron (*6*) for XeF_2. The structure was refined with the least squares program of Busing *et al.* (*7*) to the values $R = 0.053$ and $wR = 0.058$ for the agreement index and the weighted agreement index, with a single isotropic thermal parameter, B. A comparison of the observed and calculated structure factors is given in Table 1. The final parameters are $x = 0.2909$ (0.0032) and $B = 2.54$ (0.16) Å^2, where the

Table 1. Observed and calculated structure factors, F_o and F_c, for KrF_2.

hkl	F_o	F_c	*hkl*	F_o	F_c
011	107	105	222	85	85
022	52	52	233	34	36
033	64	67	244	25	24
044	36	37	311	22	17
111	51	49	322	7	6
122	23	15	333	7	5
133	16	12	400	57	59
144	7	7	411	49	45
200	61	59	422	35	32
211	91	96	433	29	29