In pure water, plots of the equivalent conductance *vs.* the square root of concentration were identical within an average deviation of about 0.02% for the four separately prepared samples of $Co(en)_3I_3$. For the comparison of the conductances of *d*- and *l*-$Co(en)_3I_3$ in the sodium tartrate–water solvent, it was found convenient to define a function P, the apparent equivalent conductance, as

$$P_{d,l} = \frac{[\kappa_{d,l}(\text{solution}) - \kappa(\text{solvent})] \times 1000}{c}$$

where $\kappa_{d,l}$ (solution) is the measured specific conductance of a solution of *d*- or *l*-$Co(en)_3I_3$ at a concentration c (equivalents per liter) dissolved in the sodium tartrate–water solvent. The measured specific conductance of the pure sodium tartrate–water stock solvent is denoted κ (solvent). This function is the same as that for the usual definition of equivalent conductance, although in this case the solvent contributes quite significantly (from approximately 40 to 80%) to the total conductance. Even though the conductances of $Co(en)_3I_3$ and solvent are definitely not additive for this system, a plot of P *vs.* $c^{1/2}$ gives an accurate graphical comparison of the conductances of the two cobalt antipodes, since exactly the same solvent composition was used for each cobalt isomer. This plot would yield identical curves for the *d*- and *l*-$Co(en)_3I_3$ salts if there were no difference in their conductance behavior. The function P will, however, readily reveal differences in conductance between the two cobalt complex ions.

To correct for any racemization, one writes

$$P'_d = P_dX'_d + P_lX'_l \text{ and } P''_l = P_dX''_d + P_lX''_l$$

where P'_d is the measured P for the predominantly *d* cobalt salt sample, and P''_l is the measured P for the predominantly *l* cobalt salt sample, and X'_d, X'_l and X''_d, X''_l are mole fractions of *d*- and *l*-$Co(en)_3I_3$ isomers in the corresponding samples. The equations are then solved for P_d and P_l.

In Fig. 1 is shown a plot of P *vs.* $c^{1/2}$ for all samples of *d*- and *l*-$Co(en)_3I_3$ in 0.003 *M* sodium *d*-tartrate. The data for both the *d*-$Co(en)_3I_3$ samples are represented by curve D–D and the data for both *l* samples by L–D within an average deviation of about 0.04%. This excellent agreement confirms both the experimental technique and the method of correcting P for partial racemization. The most notable feature of Fig. 1 is that the essentially parallel plots differ by approximately 1.3 P units or 1.7%. This difference, which is much larger than the estimated maximum experimental error of 0.1%, definitely establishes that the mobility of *l*-$Co(en)_3I_3$ is greater than that of the corresponding *d* isomer in sodium *d*-tartrate aqueous solution. Thus, we may write the inequality D–D > L–D to represent the order of specific interactions in solution. Since such an inequality should remain valid when all ions are replaced by their optical antipodes, one would predict that L–L > D–L. To verify this, samples d_1 and l_1 were run in 0.003 *M* sodium *l*-tartrate. Here the mobility of the *d* isomer was indeed greater than that of the *l* isomer, and the magnitude of the effect (1.6%) was identical within experimental error with the difference for the sodium *d*-tartrate solution.

It is interesting to note that the solubility of the D–D compound is much less than for L–D, in fact, this is the way the salts are resolved.[2] This solubility difference may well be related to our results which show a sizable preferential interaction even in dilute solution.

The data on which these curves were based as well as further work now in progress will be presented in a later publication. It is hoped that these systems will serve as models for some instances of specific interaction among the more complex molecules found in biological systems.[4]

Acknowledgment.—We thank the National Science Foundation and the National Institutes of Health for financial support for this research and gratefully acknowledge encouragement and advice from Professors Raymond M. Fuoss and Basil G. Anex.

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Mössbauer Effect in *cis–trans* Isomers

Sir:

The study of resonant γ-ray spectroscopy (Mössbauer effect) has recently been extended to a number of closely related metal–organic compounds, especially those of iron[1,2] and tin.[3] The large amounts of data which have become available from these studies have been subjected to a number of correlations, such as that between quadrupole splitting (Q.S.) and isomer shift (I.S.) of Pettit and Collins,[4] and that of Herber, King, and Wertheim[5] which suggested that the isomer shift for iron–organic compounds could be treated as an additive molecular parameter. A prediction implicit in the latter interpretation is that the observed isomer shifts for iron atoms having the same local (nearest neighbor) environment but with different molecular structure in two or more compounds should be identical.

To test this prediction, we have examined the Mössbauer spectra of two *cis–trans* isomeric pairs. The experimental details are essentially identical with those reported earlier.[1,5] The source was prepared by diffusing previously electroplated Co^{57} into metallic copper for 3 hr. at 920–950°. This source showed an isomer shift of -0.374 ± 0.010 mm. sec.$^{-1}$ for an absorber of 0.5 mil 302 stainless steel at room temperature and -0.564 ± 0.010 mm. sec.$^{-1}$ for an absorber of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ at room temperature. The motion was calibrated from the hyperfine spectrum[6] obtained using a 1.0 mil metallic iron absorber. The zero velocity point was determined from an independent Mössbauer experiment using a $Sn^{119m}O_2$

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TABLE I

MÖSSBAUER DATA FOR *cis-trans* ISOMERIC PAIRS [Cu(Co^{57})] SOURCE AT ROOM TEMPERATURE

Compound	Temp., °K.	Effect, %	Q.S., mm. sec.$^{-1}$	I.S., mm. sec.$^{-1}$	Shift from $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, mm. sec.$^{-1}$
cis-$\{C_5H_5FeCOP(C_6H_5)\}_2$	78	12	1.60 ± 0.05	−0.04 ± 0.05	+0.52 ± 0.05
trans-$\{C_5H_5FeCOP(C_6H_5)_2\}_2$	78	9	1.66 ± 0.05	−0.04 ± 0.05	+0.52 ± 0.05
cis-$\{C_5H_5FeCOAs(CH_3)_2\}_2$	78	3	1.42 ± 0.05	+0.05 ± 0.05	+0.61 ± 0.05
trans-$\{C_5H_5FeCOAs(CH_3)_2\}_2$	78	3	1.57 ± 0.05	+0.05 ± 0.05	+0.61 ± 0.05

source and an SnO_2 absorber, both at room temperature.

The two absorber pairs used were *cis*- and *trans*-$\{C_5H_5FeCOP(C_6H_5)_2\}_2$ and *cis*- and *trans*-$\{C_5H_5FeCOAs(CH_3)_2\}_2$ synthesized by methods described elsewhere.[7] The infrared spectra of these compounds in CS_2 solution all show a single absorption band in the region 1900 to 1950 cm.$^{-1}$ which is ascribed to a terminal carbonyl group, and no absorption in the bridging carbonyl region. The dimeric and diamagnetic nature of these compounds leads to the conclusion that the two iron atoms are joined by two bridging phosphorus (or arsenic) atoms, and from the resultant nearly tetrahedral environment around the iron atom it is seen that *cis* and *trans* isomers can be formulated. The assignment of configuration is based largely on proton nuclear magnetic resonance data, which show, for example, a single methyl resonance for *trans*-$\{C_5H_5FeCOAs(CH_3)_2\}_2$ and two methyl resonances for the *cis* isomer.

As has been previously noted, organometallic iron compounds do not show an appreciable resonance effect at room temperature, presumably due to the fact that the Debye temperature of these compounds is well below 300°K. For this reason, the present samples were examined at liquid nitrogen temperature in the usual transmission geometry.

The Mössbauer data at 78°K are summarized in Table I. In each case two well-defined peaks of essentially equal intensity were observed, from which it is concluded that the Gol'danskii effect[8] in these compounds is of only minor importance. From these data it is also evident that the isomer shift is identical for the *cis* and *trans* compounds within the limits of accuracy of the experiment, in consonance with the requirements of the partial isomer shift correlation previously reported.[5] The indicated error of ±0.05 mm. sec.$^{-1}$ represents an uncertainty of about 0.6 channel in the position of each of the two resonance maxima required to define the isomer shift or the shift from the centroid of the spectrum of the standard. The small shift from zero velocity arises from the particular choice of a host matrix for the Co^{57} activity and is thus not related directly to the magnitude of the error in the position of the resonance maximum. Recent comparison studies[9] have shown that nominally identical sources of Co^{57} diffused into copper are not identical with respect to their isomer shifts from zero velocity for a given absorber. We have therefore included in the last column of Table I the apparent isomer shift from the center of the $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ spectrum as an additional reference point. These data should permit the direct comparison of the present data with those obtained using other recoil-free sources of Co^{57}.

Moreover, using the relationship between the nuclear magnetic resonance shift of the cyclopentadienyl protons in CS_2 [with respect to an internal standard of $(CH_3)_4Si$] and the partial isomer shift appropriate for the cyclopentadienyl group,[5] it is possible to calculate a value for the partial isomer shift for a bridging phosphorus atom. This value is −0.010 mm. sec.$^{-1}$ for the *cis* isomer and −0.020 mm. sec.$^{-1}$ for the *trans* isomer, in good agreement with that calculated earlier.[5] A similar calculation for the arsine bridged compounds yields a value of −0.04 mm. sec.$^{-1}$ for both the *cis* and the *trans* isomer. The apparent reversal in the isomer shifts—that is, the fact that the phosphorus bridged compounds with more negative isomer shifts than the arsenic bridged compounds give rise to less negative partial isomer shifts of the bridging groups—is due to the difference in the cyclopentadienyl proton n.m.r. shifts and hence to the relative value of the appropriate partial isomer shift of the cyclopentadienyl group.

The absorbers used in this work were made up to have essentially the same quantity of Fe^{57} per unit area, and thus the magnitudes of the resonance effect should be directly comparable. From the data in Table I it is seen that the resonance effect in the arsenic compounds is lower by a factor of 3–4 than that in the analogous phosphorus compounds. This effect is due to the strong K-edge absorption of the 14.4 kev. γ-ray of Fe^{57} by arsenic, and thus high-precision data on arsenic-containing compounds are difficult to obtain since long periods of data accumulation (with the concomitant problems of electronic drift) are required to achieve good counting statistics. For this reason the present data are being extended to related antimony compounds in a further test of the additivity of partial isomer shifts in Mössbauer spectra of iron–organic compounds.

Acknowledgment.—The continued support of the U. S. Atomic Energy Commission is hereby gratefully acknowledged.

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(9) The authors are indebted to Dr. G. K. Wertheim and Professor R. L. Collins for data regarding their Cu(Co^{57}) sources prior to publication.

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Chimonanthine. A One-Step Synthesis and Biosynthetic Model

Sir:

The suggested[1,2] biosynthesis of the calycanthaceous alkaloids is represented by an oxidative dimerization of N-methyltryptamine (II), itself a natural product (dipterin[3]). The various members of the group are derivable from the tetraaminodialdehyde (IV). However, the dimer (III) would be expected to yield chimonanthine (I) directly in conditions unfavorable to hydrolytic cleavage of the indolenine or di-(N-acetal) groupings. Thus by achieving the much sought β,β′-radical coupling of the indole nucleus, we are now able

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