In the first approximation, these compounds have an appreciable uncompensated charge, in contrast, for example, to 1,5-difluoro-1,1,1,3,3,5,5-hexanitropentane, which was calculated in the same approximation and which has the symmetry of an open carbon chain (approximately local symmetry C_2) [1].

CONCLUSIONS

1. The compound 1,1,1,3,5,5,5-heptanitropentane has been prepared, and from this, 3-fluoro-1,1,1,3,5,5,5-heptanitropentane has been synthesized.

2. By means of x-ray structure analysis, a closed-chain conformation of the carbon atoms has been established for 1,1,1,3,5,5,5-heptanitropentane, 3-fluoro-1,1,1,3,5,5,5-heptanitropentane, and 3-chloro-1,1,1,3,5,5,5-heptanitropentane.

3. Calculations of the electronic structure of all three compounds showed that the 3-chloro-1,1,1,3,5,5,5-heptanitropentane is more strongly polarized, and this should lead to an increase in the electrostatic intermolecular interaction in the crystal. The distribution of averaged contacts of different types in the crystals of these compounds corresponds to their electronic structure.

LITERATURE CITED

1. L. O. Atovmyan, N. I. Golovina, L. T. Eremenko, N. G. Zhitomirskaya, F. V. Oreshko, and M. A. Fadeev, Izv. Akad. Nauk SSSR, Ser. Khim., 543 (1983).
2. N. I. Golovina and L. O. Atovmyan, "Intermolecular interactions and density of polynitro compounds," Summaries of Papers from 3rd All-Union Conference on Organic Crystal Chemistry [in Russian], Gor'kii (1981).
3. L. T. Eremenko, G. V. Oreshko, M. A. Fadeev, and N. G. Zhitomirskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2163 (1982).

IR SPECTROSCOPIC STUDY OF MATRIX-ISOLATED FREE ALLYL RADICALS AND ANALYSIS OF VIBRATIONAL SPECTRA AND STRUCTURE OF π-ALLYL ORGANOMETALLIC COMPOUNDS

A. K. Mal'tsev, V. A. Korolev,
and O. M. Nefedov

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The matrix isolation method [1] offers the unique possibility of stabilization and direct IR spectroscopic study of highly reactive free radicals, carbenes, and other species with the aim of determining their structures [2, 3] and the mechanisms of reactions in which they take part [2]. The IR spectrum of the free allyl radical (AR), which is the simplest delocalized π-system with equalized carbon–carbon bonds [4, 5], is of particular importance because of the existence of a broad class of organometallic compounds (substances of practical importance) with compositions including the π-allyl ligand C_3H_5.

The character of the chemical bond and the changes in structure of the allyl system when a π-complex is formed can be evaluated by comparing the physicochemical characteristics of the free AR and the π-allyl ligand. A good experimental base for such an analysis might be found in vibrational spectroscopy, since the known ESR [6-8], photoelectron [9], and mass spectra (see [10] and literature cited therein) of the free AR are difficult to compare with the properties of the stable complexes. It is specifically the change in vibrational frequencies of the ligand, including a decrease of 100-200 cm^{-1} in $\nu(C{=}C)$, that are characteristic for the formation of π-complexes of unsaturated compounds [11]. However, spectral data for a variety of π-allyl complexes have not been subjected to such an analysis, since the IR spectrum of the free AR had not been obtained up until quite recently.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.

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TABLE 1. Products from Pyrolysis (900°C, 10^{-3} to 10^{-4} torr) of 1,5-Hexadiene C_6H_{10}, in an Argon Matrix at 12°K

Frequency, cm^{-1}	Assignment	Frequency, cm^{-1}	Assignment
3107	$\cdot C_3H_5$	1388,5 1385	$\cdot C_3H_5$
3084	C_6H_{10}	1317	$\cdot C_3H_5$
3051	$\cdot C_3H_5$	1284	$\cdot C_3H_5$
3040	$\cdot C_3H_5$	1247	C_6H_{10}
3019	$\cdot C_3H_5$	1242	$\cdot C_3H_5$
2987	C_6H_{10}	1182,5	$\cdot C_3H_5$
2933	C_6H_{10}	1177	$CH_2{=}C{=}CH_2$
2913	C_6H_{10}	1082 1075	Impurity
2860	C_6H_{10}	995,0	C_6H_{10}
2849	C_6H_{10}	983,2	$\cdot C_3H_5$
1954,5	$CH_2{=}C{=}CH_2$	972,8	$\cdot C_3H_5$
1830 1827	C_6H_{10}	913,8	C_6H_{10}
1649	C_6H_{10}	837,0	$CH_2{=}C{=}CH_2$
1623	H_2O	808,5	$\cdot C_3H_5$
1608	H_2O	801,2	$\cdot C_3H_5$
1602	$\cdot C_3H_5$	735,0	C_2H_2
1477	$\cdot C_3H_5$	663,0 661,9	CO_2
1463 1461	$\cdot C_3H_5$	640–655	C_6H_{10}
1454	C_6H_{10}	629,0	$CH_3C{\equiv}CH$
1439 1435	C_6H_{10}	616,0	$\cdot CH_3$?
1420 1415	C_6H_{10}	510,0	$\cdot C_3H_5$

In 1982, we succeeded for the first time in registering an intense IR spectrum of AR stabilized from the gas phase in an argon matrix at 12°K. We reported 16 vibrational frequencies of the AR, which was obtained by vacuum pyrolysis of various allyl-containing compounds [12]. In 1983, researchers in West Germany [13, 14] published an IR spectrum of AR stabilized by the same mehtod, coinciding to a great degree with our data [12]. However, the interpretation of this spectrum given in [14] was not backed up by the isotope frequency shifts and vibrational calculations that are required for assignment. It is significant that a later *ab initio* calculation of the structure and approximate vibrational spectrum of AR [15] gave substantially lower frequencies $\nu_{as}(CCC)$ 1204 cm^{-1} and $\nu_s(CCC)$ 1097 cm^{-1}, in comparison with 1477 and 1242 cm^{-1} in [14]. Thus, the available experimentally determined IR spectra of AR [12, 14] require additional isotopic data and a comparison with vibrational calculations in order to determine the complete spectrum of normal vibrations of this species.

In the work reported here, we have established the frequencies of normal vibrations of the AR on the basis of the IR spectra of C_3H_5 and its deuterated analog C_3D_5 and a theoretical calculation of the complete vibrational spectrum; also, we have determined the force field of the AR. On this basis, we have carried out a comparative analysis of the spectra of the free AR and the allyl ligand in π-complexes with the aim of revealing the features of chemical bonding in the formation of these complexes.

EXPERIMENTAL

The free allyl ligand (AR) was generated in the gas phase by high-vacuum pyrolysis of compounds AllX (X = Cl, Br, I, $SiMe_3$, All) at 600-1000°C and a pressure of 10^{-1} to 10^{-4} torr in a single-pass quartz reactor, 120 × 5 mm, connected to an optical helium cryostat

$$\mathrm{AllX} \xrightarrow{600-1000^\circ} \mathrm{All} + \mathrm{X}$$

$$\mathrm{X} = \mathrm{Cl},\ \mathrm{Br},\ \mathrm{I},\ \mathrm{SiMe_3},\ \mathrm{All}$$

The pyrolyzed products were frozen, together with excess argon, on a CsI substrate, chilled to 12°K by means of a cryogenic system with a closed cycle. The IR spectra were recorded by means of a Hitachi–Perkin-Elmer Model 225 spectrophotometer.

In the matrix IR spectra of the products from the pyrolysis of the compounds AllX, we observed and assigned to AR the bands indicated in Tables 1 and 2, which we have reported

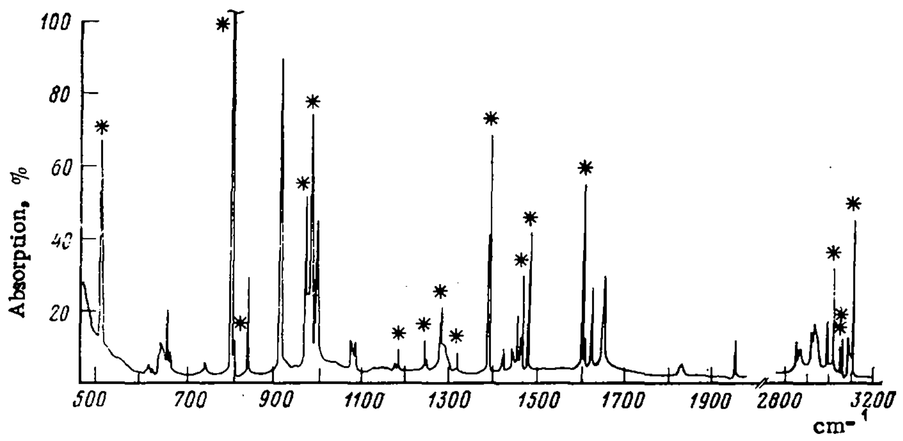


Fig. 1. IR spectrum of products from pyrolysis of 1,5-hexadiene (900°C, 10^{-4} torr), in Ar matrix at 12°K (* — $\overline{CH_2{-}CH{-}CH_2}$).

previously [12]. The positions and relative intensities of the bands coincided when the C_3H_5 was obtained from different starting compounds. In Figs. 1 and 2 we show the spectra of the products from pyrolysis of 1,5-hexadiene and AllI; and in Tables 1 and 2 we have listed the frequencies of all the compounds formed in the pyrolysis. In the process of controlled warm-up of the matrix from 12° to 40°K, there was a synchronous decrease in the intensities of these bands with a simultaneous increase in intensity of the bands pertaining to diallyl, the known product of AR recombination.

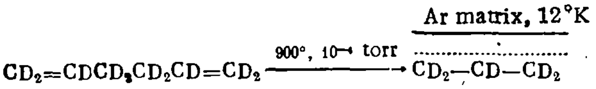
Of the starting compounds that we have examined, the 1,5-hexadiene dissociates the most selectively with the highest yields of AR. Therefore, in preparing the deuterated AR, we synthesized a sample of perdeutero-1,5-hexadiene through the reaction

$$ClCD_2CD{=}CD_2 + Mg \xrightarrow{\text{ether}\ ,\ 34^\circ} CD_2{=}CDCD_2CD_2CD{=}CD_2$$

The mass spectrum of the C_6D_{10} showed a good correspondence with the known pattern of fragmentation of 1,5-hexadiene under electron impact (50 eV), with the following values of m/z (relative intensities in parentheses): 92(7) $[C_6D_{10}]^+$, 90(6) $[C_6D_9]^+$, 74(100) $[C_5D_7]^+$, 60(65) $[C_4D_6]^+$, 58(7) $[C_4D_5]^+$, 46(88) $[C_3D_5]^+$, 44(8) $[C_3D_4]^+$, 43(65) $[C_3D_3]^+$, 32(14) $[C_2D_4]^+$, 30(26) $[C_2D_3]^+$).

The matrix IR spectrum of C_6D_{10}, which is shown in Fig. 3 along with the spectrum of C_6H_{10}, contains bands in the region typical for C—D stretching vibrations, including bands at 2250, 2210, and 2202 cm^{-1}, corresponding to the ν(C—D) vibrations in the $CD{=}CD_2$ group. The band at 1589 cm^{-1} confirms the presence of C=C bonds in the molecule. On the whole, the bands of the C_6D_{10} are shifted regularly in relation to the spectrum of C_6H_{10}, towards lower frequencies.

In the matrix IR spectrum of products from vacuum pyrolysis of C_6D_{10} (900°C, 10^{-4} torr), there are eight rather intense bands at 2285, 2214, 2209, 1263, 1062, 1018, 1007, and 646.5 cm^{-1}, which we have assigned to deuterated AR (Fig. 4).



$$CD_2{=}CDCD_2CD_2CD{=}CD_2 \xrightarrow{900^\circ,\ 10^{-4}\ \text{torr}} \overline{CD_2{-}CD{-}CD_2}$$

Ar matrix, 12°K

Upon warming the Ar matrix from 12° to 40°K, these bands become weaker and then disappear. The weak bands at 768, 762, and 650 cm^{-1}, which disappear when the matrix is warmed, may also pertain to the radical C_3D_5 (Table 3). In addition to C_3D_5, the pyrolysis of C_6D_{10} forms propylene-d_6, allene-d_4, and methylacetylene-d_4, analogous to the pyrolysis of nondeuterated 1,5-hexadiene (see Table 3).

The experimentally determined IR spectra of C_3H_5 and C_3D_5 (Table 4) have enabled us to carry out a soundly based theoretical calculation in order to refine the assignment of the observed bands to the normal vibrations of the AR and to determine the force field of this species.

The calculation of the vibrational spectra by means of the set of programs given in [16] was performed for a planar model of the AR with r_{CC} = 1.40 Å and r_{CH} = 1.09 Å; all angles were

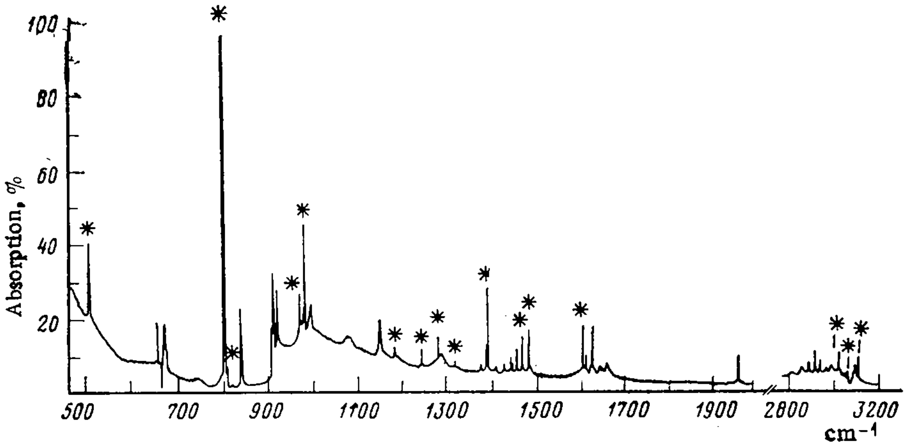


Fig. 2. IR spectrum of products from pyrolysis of C_3H_5I (800°C, 10^{-4} torr), in Ar matrix at 12°K ($\overset{\bullet}{\overline{-CH_2-CH-CH_2}}$).

taken as 120°. The initial values of the force constants were carried over from molecules of olefins, benzene [17], and π-allyl complexes [18]. The AR, having symmetry C_{2v} [4, 7], must have 18 normal vibrations of the types $7A_1 + 2A_2 + 3B_1 + 6B_2$, of which 16 (all except those belonging to type A_2, one torsional and one wagging vibration of the CH_2 group) are active in the IR spectrum. The results from calculations for the C_3H_5 and C_3D_5 radicals are presented in Table 4. In solving the reverse vibrational problem, the force constants were refined by an iteration procedure by the least-squares method [16].

DISCUSSION OF RESULTS

Assignment of IR Bands to Normal Vibrations of AR

In analyzing the spectra that were obtained, beginning with the low-frequency vibrations, we note that in the region of C—H stretching vibrations, where the AR has five normal vibrations ($3A_1 + 2B_2$), we registered four bands in the spectrum of C_3H_5 and three bands of C—D vibrations in the spectrum of C_3D_5. A comparison of the positions of these bands with the results obtained by calculation (Table 4) enabled us to assign the 3051 cm^{-1} band to ν(CH) (in [14], 3048 cm^{-1}).

On a background of weak bands at 1622, 1608, and 1590 cm^{-1} from impurity molecules of H_2O in the matrix, we found in the spectrum of the C_3H_5 a medium-intensity band at 1602 cm^{-1}, which is regarded as an overtone of the most intense band of the AR at 801.2 cm^{-1}. Also assigned to combination vibrations are the weak bands of the AR at 1317, 1182, and 3040 cm^{-1}.

In assigning the IR bands that we registered below 1500 cm^{-1}, it was taken into account that for the π-allyl ligand in the 1350-1500 cm^{-1} region, synphase and antiphase deformation (scissoring) vibrations of CH_2 groups and a stretching vibration ν_{as}(CCC) have been observed [11]. As shown by the calculations, as a result of replacement of the H atoms by D, the frequencies of these deformation vibrations of the AR should be shifted by 400-450 cm^{-1}, to frequencies of 1000-1100 cm^{-1}, whereas ν_{as}(CCC) decreases only very slightly. The literature data confirm that for molecules of completely deuterated hydrocarbons, all of the deformation vibrations lie below 1150 cm^{-1} [17]. Therefore, the IR band at 1263 cm^{-1}, the only band in the 1150-1500 cm^{-1} region in the spectrum of the C_3D_5, must pertain to ν_{as}(CCC). For the C_3H_5, the calculated frequency corresponding to this vibration is somewhat higher. In the observed spectrum of C_3H_5 in this region, there is a band at 1284 cm^{-1}, which has been assigned to ν_{as}(CCC). A calculation of the contributions of the vibrational coordinates to the potential energy (see Table 4) shows that this vibration is highly characteristic, both for the C_3H_5 and the C_3D_5.

Thus, all three of the observed bands of C_3H_5 in the 1350-1500 cm^{-1} region must pertain to deformation vibrations, of which the two scissoring vibrations $\delta(CH_2)$ usually have the highest frequency. According to the calculations, they differ by only 20-30 cm^{-1}. Therefore, we will assign to the antiphase vibration $\delta(CH_2)$ the band at 1477 cm^{-1}, and to the synphase vibration the band at 1463 cm^{-1}. In the IR spectrum of the C_3D_5, according to the calculations, these correspond to the bands at 1062 and 1018 cm^{-1}. The third band, at 1388.5 cm^{-1},

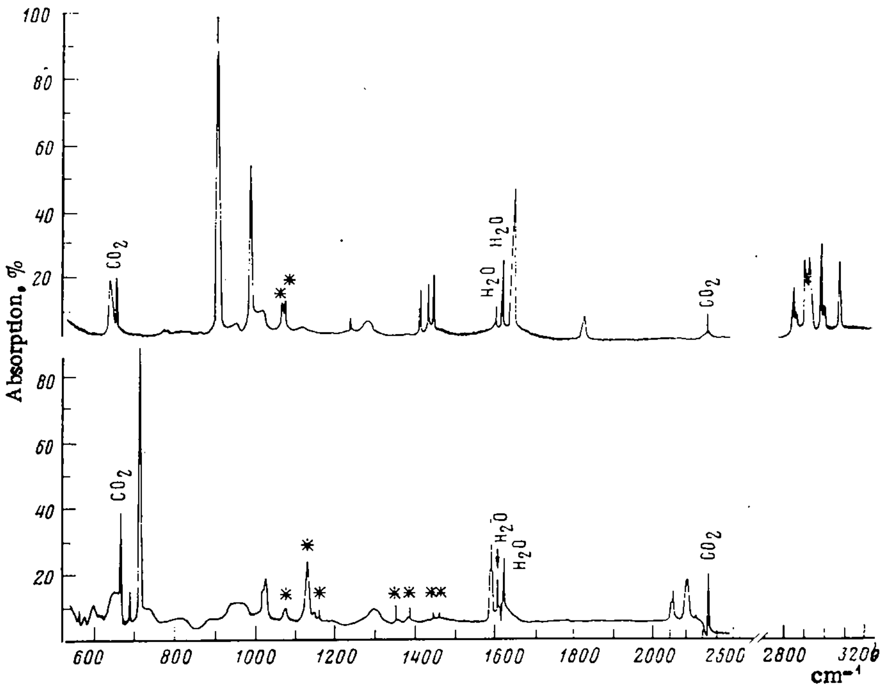


Fig. 3. IR spectra (Ar matrix, 12°K): a) 1,5-hexadiene; b) 1,5-hexadiene-d_{10} (* — impurity).

can be assigned to the in-plane vibration δ(CH) of the B_2 type, which according to the data of our calculation and *ab initio* calculations [15], is 70÷100 cm^{-1} lower in frequency than the $\delta(CH_2)$ vibration. Upon deuteration, the shift of this band may be almost as great as 400 cm^{-1}; therefore, to δ(CD) for the C_3D_5 we have assigned the band at 1007 cm^{-1}. The potential energy distribution (PED, see Table 4), shows that a significant contribution is made to this vibration by the coordinates $\alpha(CH_2)$ and $\beta(CH_2)$. This may be the reason for the higher value of the frequency δ(CH) for the C_3H_5 in comparison with certain unsaturated compounds, such as propylene with δ(CH) 1297 cm^{-1}, diallylwith 1301 cm^{-1}, and methylallene with 1330 cm^{-1} [17]. On the other hand, for cis-disubstituted ethylenes, the frequency of the in-plane deformation vibration δ(CH) amounts to 1400-1405 cm^{-1}, and for trisubstituted ethylenes 1375-1390 cm^{-1} [19, pp. 80-81]; in particular, for cis-2-butene, the frequency δ(CH) of the B_2 type is 1420 cm^{-1} [17, p. 231], i.e., still higher than the proposed value of 1389 cm^{-1} for the AR.

Additional evidence in favor of the assignment of the 1389 cm^{-1} band to δ(CH) can be obtained by analyzing the vibrations of the π-allyl ligand in complexes, in the spectra of which there is always an intense band near 1380 cm^{-1}, depolarized in the Raman spectra and corresponding to symmetry A" [11]. However, when the H atom on the central carbon atom of the π-allyl ligand is replaced by Cl [20] or Br [21], this band does not appear in the spectra; and for the ligand π-2-MeC_3H_4, the 1386 cm^{-1} band pertains to a different vibration, since it is polarized in the Raman spectrum [22]. Hence it is possible that the band close to 1380 cm^{-1} for the π-C_3H_5 ligand corresponds to the δ(CH) vibration and that it is shifted to 1389 cm^{-1} for the AR.

The symmetrical stretching skeletal vibration ν_s(CCC), as shown by our calculations, is strongly mixed with the deformation rocking vibration $\delta_r(CH_2)$, the difference in their frequencies amounting to about 200 cm^{-1}. In the spectrum of the C_3H_5 we observe a band at 1242 cm^{-1} and two bands close to 1000 cm^{-1}, one of which, at 972.8 cm^{-1}, we will arbitrarily assign to ν_s(CCC) and the other, at 983.2 cm^{-1}, to the antiphase vibration $\delta_r(CH_2)$. Since the data for the π-allyl complexes [23, 24] indicate that the synphase vibration $\delta_r(CH_2)$ may be in the 1200 cm^{-1} region, we are regarding the 1242 cm^{-1} band as $\delta_r(CH_2)$. However, in view of the mixing of the vibrations ν_s(CCC) and $\delta_r(CH_2)$, the reverse assignment may be possible, i.e., the 1242 cm^{-1} band to ν_s(CCC) and the 972.8 cm^{-1} band to $\delta_r(CH_2)$. An analysis of the spectra of 1-alkenes [17] confirms (in contrast to [14]) that the vibrations $\delta_r(CH_2)$ usually have a lower frequency than δ(CH).

In the region below 1000 cm^{-1} we usually find the bands of out-of-plane deformation vibrations; for the IR spectra of molecules with terminal $=CH_2$ groups, an extremely intense wagging

TABLE 2. Products from Pyrolysis (800°C*, 10^{-4} torr) of C_3H_5I, in Argon Matrix at 12°K

Frequency, cm^{-1}	Assignment	Frequency, cm^{-1}	Assignment
3107	$\cdot C_3H_5$	1373	C_3H_6
3089	C_3H_6, C_6H_{10}	1318	$\cdot C_3H_5$
3050	$\cdot C_3H_5$	1284	$\cdot C_3H_5$
3017	$\cdot C_3H_5$	1242	$\cdot C_3H_5$
2980	C_3H_6	1190	C_3H_5I
2938	C_3H_6, C_6H_{10}	1182	$\cdot C_3H_5$
2920	C_3H_6	1152	C_3H_5I
2886	C_3H_6	995,0	C_3H_6
1954	$CH_2{=}C{=}CH_2$	983.2	$\cdot C_3H_5$, C_3H_5I
1650	C_3H_6, C_6H_{10}	972,7	$\cdot C_3H_5$
1623	H_2O	919,7	C_3H_5I
1608		913.6	C_6H_{10}
1602	$\cdot C_3H_5$	908,5	C_3H_6
1477	$\cdot C_3H_5$	837,0	$CH_2{=}C{=}CH_2$
1463	$\cdot C_3H_5$	808,0	$\cdot C_3H_5$
1453	C_3H_6, C_6H_{10}	801,2	$\cdot C_3H_5$
1439	C_3H_6, C_6H_{10}	675,0	C_3H_5I
1406	C_3H_5I	663,0	CO_2
1389	$\cdot C_3H_5$	661,9	
1385		509,5	$\cdot C_3H_5$

*In the 2800-3200 cm^{-1} region, we have listed the frequencies of the products from pyrolysis of C_3H_5I at 1000°C.

vibration $\rho_w(CH_2)$ is characteristic. The assignment of the most intense band in the spectrum of C_3H_5 at 801.2 cm^{-1} (in the spectrum of C_3D_5 at 646.5 cm^{-1}) to one of the two vibrations $\rho_w(CH_2)$ of type B_1 is quite reliable, since precisely such an isotopic shift is predicted by calculation. The vibration $\rho_w(CH_2)$ of type A_2 is inactive in the IR spectrum.

Moreover, it is known that the band $\rho_w(CH_2)$ for allenes and vinyl derivatives is accompanied by a band in the overtone region, distinguished by a remarkably high intensity, with a frequency that coincides almost exactly with the doubled frequency of the fundamental vibration [25, p. 74; 19, pp. 76-78]. Just such a band at 1602 (2 × 801) cm^{-1} is observed in the spectrum of C_3H_5, which confirms the assignment of the 801.2 cm^{-1} band to $\rho_w(CH_2)$. The much lowered value of the frequency of $\rho_w(CH_2)$ for the AR in comparison with vinyl and vinylidene hydrocarbons, for which $\rho_w(CH_2)$ has a frequency of 880-920 cm^{-1}, is the first example that has been found of the influence of conjugation and delocalization in AR on the frequency of this vibration [25, p. 55].

The calculated value of the frequency of the out-of-plane vibration $\rho(CH)$ proved to be almost 600 cm^{-1} below the frequency of the in-plane vibration $\delta(CH)$, to which we have assigned the band at 1389 cm^{-1}. Such a difference in frequencies has been predicted by an *ab initio* calculation [15], and also by calculation of the spectrum of the π-allyl ligand [26]. Therefore, we have assigned to $\rho(CH)$ the weak band at 808.5 cm^{-1}, which was not included in the initial list [12] of frequencies of C_3H_5, but was reported in [13, 14]. Let us note that a large difference between the frequencies of $\delta(CH)$ and $\rho(CH)$ has been noted for many 1-alkenes, the values of $\rho(CH)$ being 578 cm^{-1} for propylene, 623 for 1-butene, 673 and 880 for trans-2-butene, and 808 for trimethylethylene [17]; i.e., this vibration is not characterized by a constant frequency of 950-1000 cm^{-1} as was supposed by Maier et al. [14], who assigned to this vibration the band of AR at 985 cm^{-1}. Nonetheless, the assignment of the 808.5 cm^{-1} band to the vibration $\rho(CH)$ of the AR is not completely reliable, because of its low intensity and the large deviation from the calculated value.

The deformation skeletal vibration $\delta(CCC)$ for π-allyl complexes is usually located in the 505-560 cm^{-1} region [11]. Therefore, we have assigned to this vibration the IR band at 510.0 cm^{-1} in the spectrum of C_3H_5, the only band located in the region below 800 cm^{-1}. Upon deuteration, this frequency should be lowered by 80-100 cm^{-1}; however, in the spectrum of C_3D_5, we did not observe any bands in the 400-500 cm^{-1} region. This may indicate a possible assignment of the 510 cm^{-1} band to a different deformation vibration, for example the torsional vibration $\rho_t(CH_2)$; or it may indicate a sharp decrease in band intensity upon deuteration; or, finally, it may indicate a large decrease in frequency of this vibration for C_3D_5 as a result of mixing with other vibrations.

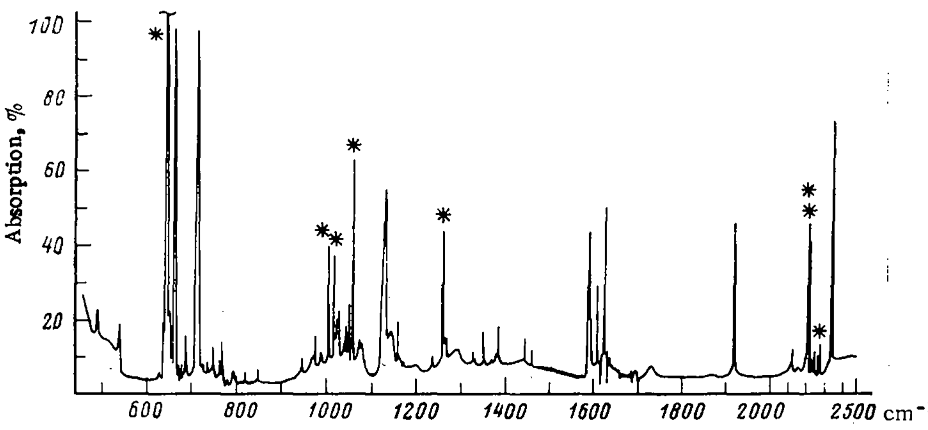


Fig. 4. IR spectrum of products from pyrolysis of 1,5-hexadiene-d_{10} (920°C, 10^{-4} torr), in Ar matrix at 12°K (*—$\overline{CD_2\text{—}CD\text{—}CD_2}$).

The frequencies of the two torsional vibrations $\rho_t(CH_2)$ of types A_2 and B_1 should correspond in general to the magnitude of the rotation barrier in the AR, 15.7 kcal/mole [8], and they should be intermediate in comparison with the frequencies of the torsional vibrations around C—C bonds (278 cm^{-1} for ethane, rotation barrier 2.93 kcal/mole [27]) and around C═C bonds (1024 cm^{-1} for ethylene [17], rotation barrier 65 kcal/mole [28, 29]). In accordance with an *ab initio* calculation [15], we will assume that for the AR, the high-frequency torsional vibration is the antiphase type A_2, and the low-frequency is the synphase type B_1. The frequencies of these vibrations, according to our calculations, will be located in the region below 400 cm^{-1}, i.e., outside the range of the measurements.

Thus, the spectrum of the radical C_3D_5 (obtained for the first time) in comparison with the spectrum of C_3H_5 [12], along with the vibrational calculation performed in the present work, has provided us with grounds for a new assignment of the IR bands to the normal vibrations of the AR (see Table 4), which provides support for the conclusions of [14] only in the case of 3 of the 12 bands in the region below 1500 cm^{-1} (1463, 801, and 510 cm^{-1}).

Vibrational Frequencies of Allyl Radical and π-Allyl Ligand

The spectrum of normal vibrations of the AR that we have determined can be compared with the spectrum of the π-allyl ligand entering into the composition of numerous organometallic π-complexes [11, 18, 20-24, 26, 30-41]. We will examine separately the out-of-plane and in-plane vibrations of the AR.

Thus, the increase in frequency of the wagging vibration $\rho_w(CH_2)$ that is known for unsaturated compounds when a π-complex is formed, for example from 947 to 1023 cm^{-1} when the change is made from the ethylene molecule to Zeise's salt [42], proves to be analogous to the change in frequency of $\rho_w(CH_2)$ from 801.2 cm^{-1} in the AR to 900-950 cm^{-1} in the π-allyl complexes. Also consistent is the sharp increase in relative intensity of this vibration for the free ligand in comparison with the complex, such that the extremely strong IR bands at 801.2 cm^{-1} for the C_3H_5 and 646.5 cm^{-1} for the C_3D_5 are convenient analytical characteristics of these radicals.

Even though the IR bands of torsional vibrations $\rho_t(CH_2)$ (A_2 and B_1) cannot be detected for the AR, the values of the frequencies of $\rho_t(CH_2)$ that were obtained by calculation in the present work, and also by means of *ab initio* calculations [15], indicate that for these out-of-plane vibrations as well, the frequencies increase when the change is made from the free ligand (AR) to π-allyl complexes (910-1020 cm^{-1} [22-24, 31-33, 35]). The same picture may be followed for the out-of-plane vibrations ρ(CH), the frequency of which we have determined as 808.5 cm^{-1}, whereas for π-allyl complexes, it is usually obtained in the interval 900-1230 cm^{-1} [23, 24, 30-33, 40, 41].

On the other hand, when we compare the AR with the π-allyl complexes, attention is drawn to the relatively small change in frequencies of the in-plane vibrations. Thus, the π-allyl ligand has four planar deformation vibrations of CH_2 — scissoring $\delta(CH_2)$ and rocking $\delta_r(CH_2)$ — the band close to 1460 cm^{-1} being assigned in practically all studies to the synphase vibration $\delta(CH_2)$. At the same time, we have determined in the present work that the frequency of

TABLE 3. Products from Pyrolysis (920°C, 10^{-4} torr) of 1,5-Hexadiene-d_{10}, in Argon Matrix at 12°K*

Frequency, cm^{-1}	Assignment	Frequency, cm^{-1}	Assignment
2339	CO_2, $CD_2=C=CD_2$	1045	$CD_3C\equiv CD$
2285	$\cdot C_3D_5$	1028	$CD_2=C=CD_2$
2278	‡	1025	C_6D_{10}
2274	‡	1018	$\cdot C_3D_5$
2255	C_6D_{10}	1007	$\cdot C_3D_5$
2236	$CD_3C\equiv CD$, C_6D_{10}	993,0	‡
2214	$\cdot C_3D_5$	976,9	‡
2209	$\cdot C_3D_5$	946,5	C_2H_4
2115	C_6D_{10}	847,0	‡
1916,5	$CD_2=C=CD_2$	821,5	$CD_2=C=CD_2$?
1623	H_2O	794,2	‡
1608		767,1	†
1592		762,2	†
1589	C_6D_{10}	748,6	†?
1372	‡	738,3	C_3D_6
1328	‡	713,1	C_6D_{10}
1271	†	687,9	C_6D_{10}
1266	†	663,3	CO_2, $CD_2=C=CD_2$
1263	$\cdot C_3D_5$	650.5	†
1261		646,5	$\cdot C_3D_5$
1238	‡	640,6	†
1062	$\cdot C_3D_5$	627,0	†
1058	‡	541,7	C_2D_2
1052	C_3D_6	493,4	$CD_3C\equiv CD$

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*Not included in the table are frequencies pertaining to the impurity Et_2O.

†Frequencies pertaining to unidentified unstable species.

‡Frequencies pertaining to unidentified stable molecules.

this vibration for the AR is very similar, 1463 cm^{-1}. The frequency of the anitphase vibration $\delta(CH_2)$ for π-allyl complexes, according to the data obtained by a number of investigators [22, 24, 31, 32, 41], is in the 1480-1500 cm^{-1} range, whereas for the AR, according to our data, the frequency is 1477 cm^{-1}. For the synphase and antiphase vibrations $\delta_r(CH_2)$ of the π-complexes, corresponding values have been reported close to 1230 cm^{-1} [23, 24, 35, 11] and in the 750-940 cm^{-1} range [11]; for the AR in the present work, the frequencies are 1242 and 983 cm^{-1}.

Also regularly present in the spectra of the π-allyl complexes is the above-discussed band close to 1380 cm^{-1}, which could be compared with the frequency of the in-plane vibration of the AR $\delta(CH)$ 1389 cm^{-1}.

Finally, we should examine the vibrations of the atoms of the carbon skeleton in the allyl system, i.e., the stretching vibrations $\nu_{as}(CCC)$ and $\nu_s(CCC)$ and the deformation vibrations $\delta(CCC)$, which also take place in the plane of the molecule. The symmetric stretching vibration $\nu_s(CCC)$ of the π-allyl ligand for various complexes is located in the interval 1005-1025 cm^{-1} [11], not greatly different in frequency from the value $\nu_s(CCC)$ 973 cm^{-1} proposed in the present work for the AR. An analogous situation exists for the vibration δ (CCC): 505-560 cm^{-1} for the π-allyl ligand [11] and 510 cm^{-1} for the AR.

We may add that of the five C–H stretching vibrations [antiphase and synphase $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$, and also $\nu(CH)$], which also take place in the plane of the allyl system, the difference in frequencies between the AR and the π-allyl ligand [11] for the $\nu_{as}(CH_2)$ antiphase vibrations is no greater than 1%, and for the other four vibrations no greater than 0.5%.

Thus, if we proceed from our assignment of the AR spectrum, we find that for practically all of the out-of-plane vibrations of this species $\rho_w(CH_2)$, $\rho(CH)$, and $\rho_t(CH_2)$, the frequencies are substantially lower than for the corresponding vibrations of the π-allyl ligand in complexes, but there is little change in the in-plane vibrations $\delta(CH_2)$, $\delta_r(CH_2)$, $\delta(CH)$, $\delta(CCC)$, $\nu_s(CCC)$, $\nu_{as}(CH_2)$, $\nu_s(CH_2)$, and $\nu(CH)$. The question of changes in values of $\nu_{as}(CCC)$ upon formation of π-complexes should be examined separately.

TABLE 4. Interpretation of Vibrational Spectrum of Allyl Radical and Allyl Radical-d_5

Vibration No.	Symmetry	Approximate form of vibration	$\overline{CH_2-\dot{C}H-CH_2}$					$\overline{CD_2-\dot{C}D-CD_2}$			
			our work			[14]	[15]	our work			[15]
			ν, cm^{-1} exp.	ν, cm^{-1} calc.	form of vibration of PED, %	ν, cm^{-1} exp.	ν, cm^{-1} calc.	ν, cm^{-1} exp.	ν, cm^{-1} calc.	form of vibration of PED, %	ν, cm^{-1} calc.
1	A_1	$\nu(CH_2)$	3107	3100	q_{CH_2} (95)	3105	3412		2292	q_{CD_2} (95)	2543
13	B_2	$\nu(CH_2)$	(3107)	3079	q_{CH_2} (95)	3105	3407		2285	q_{CD_2} (100)	2538
2	A_1	$\nu(CH)$?	3051 3040	3041	q_{CH} (80), q_{CH_2} (20)	3048	3327	2285	2244	q_{CD} (92)	2459
3	A_1	$\nu(CH_2)$	3019	3009	q_{CH_2} (83), q_{CH} (12)	3019	3318	2214	2201	q_{CD_2} (90)	2409
14	B_2	$\nu(CH_2)$ 801×2	(3019) 1602	2991	q_{CH_2} (97)	3019	3314	2209	2198	q_{CD_2} (90)	2401
15	B_2	$\delta(CH_2)$	1477	1486	$\alpha^-_{CH_2}$ (41), β_{CH} (24), $\beta^-_{CH_2}$ (33)	1463	1632	1062	1091	$\alpha^-_{CD_2}$ (40), $\beta^-_{CD_2}$ (31), β_{CD} (22)	1193
4	A_1	$\delta(CH_2)$	1463	1459	$\alpha^+_{CH_2}$ (57), $\beta^+_{CH_2}$ (44)	1463	1661	1018	1053	$\alpha^+_{CD_2}$ (44), $\beta^+_{CD_2}$ (47)	1351
16	B_2	$\delta(CH)$ 510+802	1389 1317	1389	β_{CH} (77), $\alpha^-_{CH_2}$ (18), $\beta^-_{CH_2}$ (18)	1285	1556	1007	984	β_{CD} (52), $\alpha^-_{CD_2}$ (19), $\beta^-_{CD_2}$ (17)	1361
17	B_2	$\nu_{as}(CCC)$	1284	1274	$Q^-_{C=C}$ (100)	1477	1204	1263	1270	$Q^-_{C=C}$ (100)	1003
5	A_1	$\delta_r(CH_2)$?	1242 1182	1239	$\beta^+_{CH_2}$ (52), Q^+_{C-C} (36)	1403	1370		826	$\beta^+_{CD_2}$ (50), $Q^+_{C=C}$ (33)	1148
18	B_2	$\delta_r(CH_2)$	983,2	994	$\beta^-_{CH_2}$ (89), $Q^-_{C=C}$ (18)	1389	1040		757	$\beta^-_{CD_2}$ (98)	779
6	A_1	$\nu_s(CCC)$	972,8	975	$Q^+_{C=C}$ (51), $\beta^+_{CH_2}$ (49)	1242	1093		1152	$Q^+_{C=C}$ (59), $\beta^+_{CD_2}$ (26), $\alpha^+_{CD_2}$ (12)	920
10	B_1	$\rho(CH)$	808,5	915	ρ_{CH} (31), ρ_{CH_2} (38), $\chi^{CH_2}_{CCH}$ (28)	985	1051		757	ρ_{CD} (30), ρ_{CD_2} (42), $\chi^{CD_2}_{CCD}$ (25)	804
11	B_1	$\rho_w(CH_2)$	801,2	795	ρ_{CH_2} (61), ρ_{CH} (28), $\chi^{CH_2}_{CCH}$ (14)	802	786	646	596	ρ_{CD_2} (56), ρ_{CD} (34), $\chi^{CD_2}_{CCD}$ (12)	640
8	A_2	$\rho_w(CH_2)$		804	ρ_{CH_2} (100)		761		621	ρ_{CD_2} (100)	601
7	A_1	$\delta(CCC)$	510	510	γ_{CCC} (65), β_{CH} (17), β_{CH_2} (17)	510	476		420	γ_{CCC} (57), β_{CD} (15), β_{CD_2} (25)	389
9	A_2	$\rho_t(CH_2)$		281	$\chi^{CH_2}_{CCH}$ (100)		596		196	$\chi^{CD_2}_{CCD}$ (100)	424
12	B_1	$\rho_t(CH_2)$		200	$\chi^{CH_2}_{CCH}$ (59) ρ_{CH} (40)	810	562		151	$\chi^{CD_2}_{CCD}$ (63), ρ_{CD} (37)	433

Frequency of Antisymmetric Stretching Vibration and Character of Bonds C⎓C⎓C for AR

It is known that for unsaturated compounds, the vibration frequency of the C=C bond, 1600-1650 cm^{-1}, is lowered substantially upon the formation of π-complexes [42, 11], this being related to weakening of the multiple bond as a result of dative feed of electron density from the metal atom to the antibonding orbital of the ligand [43]. For π-allyl complexes of transition metals, most investigators have assigned to ν_{as}(CCC) the band in the 1480-1520 cm^{-1} region, depolarized in the Raman spectrum [11, 18, 23, 26, 33-40].

At the same time, it has been shown in the present work that the frequency ν_{as}(CCC) for the AR is 1284 cm^{-1}. Thus, if we proceed from the above-mentioned assignment for the π-allyl complexes, ν_{as}(CCC) 1480-1520 cm^{-1}, then we should examine the question of an increase in the frequency of the multiple bond of the AR upon formation of a complex. This same question is valid with the assignment to ν_{as}(CCC) of the π-allyl ligand of the band in the 1380 cm^{-1} region, as is asserted in a number of studies [22, 24, 31, 32, 41].

The increase in the frequency ν_{as}(CCC) upon formation of π-allyl complexes is opposite to the indicated relationship for unsaturated compounds. Such an increase may be explained by transfer of electron density from the metal atom upon formation of a dative bond, not to an antibonding orbital, but to a nonbonding orbital of the π-allyl system; it may also be explained by the considerably smaller role of dative transfer for the AR in comparison with σ-transfer from the ligand to vacant d-orbitals of the metal atom [44]. In this case, there cannot be a weakening of the multiple bond for the AR or a decrease in its vibrational frequency. Quite recently, an example has been reported of an increase in vibrational frequency of a ligand when the change is made from the dianion of cyclooctatetraene in K_2(cot) to the π-complex Th$(cot)_2$, which is explained by the absence of dative transfer to antibonding orbitals of the ligand in this case [45].

If the above-proposed assignment of the 1380 cm^{-1} band to the vibration δ(CH) is correct [and not to ν_{as}(CCC)], the value used alternatively in the literature for ν_{as}(CCC), 1480-1520 cm^{-1} [15, 18, 23, 26, 33-40], will differ by almost 200 cm^{-1} from the frequency found in the present work for AR, 1284 cm^{-1}. Such a difference is very large, since, according to the data of quantum-chemical calculations [4, 46], the orders of the C⎓C bonds for the AR and the ions $C_3H_5^+$ and $C_3H_5^-$ are quite similar, and their lengths differ by no more than 0.02 Å, which should not have any great effect in changing the frequency ν_{as}(CCC). Therefore, the value of ν_{as}(CCC) for the π-allyl ligand should probably be closer to 1284 cm^{-1}; thus, the assignment of the 1480-1520 cm^{-1} frequency to this vibration does require verification.

The value found by refinement of the force field of the AR for the valence-force constant $F_{C⎓C}$ 5.8 mdyne/Å (Table 5) indicates that the rigidity of the C⎓C bonds in the AR is intermediate between that of an ordinary bond ($F_{C—C}$ = 4.5 mdyne/Å) and a double bond $F_{C=C}$ = 9.0 mdyne/Å [17]). Maier et al. [14], in the IR spectrum of AR, assigned to ν_{as}(CCC) the band at 1477 cm^{-1}, and to ν_s(CCC) the band at 1242 cm^{-1}. Our calculation shows that in this case, the value of the force constant $F_{C⎓C}$ for the AR (≈7 mdyne/Å) would be close to $F_{C=C}$, whereas the energy of the π-bond for the AR (15-17 kcal/mole [8, 47]) is four times smaller than for C_2H_4. The lower values of $F_{C⎓C}$ that we obtained for the AR, and also the frequencies ν_{as}(CCC) 1284 cm^{-1} and ν_s(CCC) 972.8 cm^{-1}, are in qualitative agreement with the results from an *ab initio* calculation [15], which approximately predicts the values ν_{as}(CCC) 1204 cm^{-1} and ν_s(CCC) 1093 cm^{-1}.

The frequency of the deformation vibration δ(CCC) is related to another structural characteristic of the π-allyl system, the CCC bond angle; an increase in this angle should give an increase in the frequency δ(CCC). Values of δ(CCC) differ markedly for the π-allyl complexes of the transition metals (505-560 cm^{-1}) and for ionic compounds with a π-delocalized allyl fragment, for example C_3H_5Li (606 cm^{-1} [48]). In accordance with the theory, the CCC angle for the first, which according to data of x-ray structure analysis is 111-117° [49], is substantially smaller than for compounds of the ionic type (134° for the π-allyl system of fluorenyllithium [50]). In accordance with this relationship the frequency δ(CCC) 510 cm^{-1} that has been found for the AR indicates closeness of magnitudes of the CCC angle for this species and for π-allyl complexes of transition metals. Therefore, the structure of the π-allyl ligand in such complexes must be more similar to the AR than to the $C_3H_5^-$ anion; and upon formation of a chemical bond between the AR and the transition-metal atom no negative charge will arise in the π-allyl ligand. This is consistent with the acceptor chemical properties of the carbon atoms of the ligand in the π-complex that has been formed [51].

TABLE 5. Force Field of Free Allyl Radical

Force constants			
diagonal	mdyne • Å • rad^{-2}	interaction	mdyne • rad^{-1}
$F(\nu C \overset{\cdots}{-} C)$	5,797 *	$f(\nu C \overset{\cdots}{-} C,\ \nu C \overset{\cdots}{-} C)$	0,540 *
$F(\nu CH_2)$	5,060 *	$f(\nu C \overset{\cdots}{-} C,\ \nu CH)$	0,010 *
$F(\nu CH)$	5,080 *	$f(\nu C \overset{\cdots}{-} C,\ \nu CH)$	0,348 *
$F(\delta CH_2)$	0,411	$f(\nu C \overset{\cdots}{-} C,\ \delta_r CH_2)$	0,427
$F(\delta_r CH_2)$	0,621	$f(\nu C \overset{\cdots}{-} C,\ \delta CH)$	−0,500
$F(\delta CH)$	0,631	$f(\nu C \overset{\cdots}{-} C,\ \delta CCC)$	−0,016
$F(\delta CCC)$	1,201	$f(\nu CH_2,\ \delta CH_2)$	−0,004
$F(\rho_w CH_2)$	0,220	$f(\nu CH_2,\ \delta_r CH_2)$	0,510
$F(\rho_t CH_2)$	0,050	$f(\delta CH_2,\ \delta_r CH_2)$	−0.008
$F(\rho CH)$	0,218	$f(\rho_w CH_2,\ \rho_t CH_2)$	0,005

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*mdyne • $Å^{-1}$.

Thus, we obtain still another confirmation of our conclusion as to the absence of back-transfer of electron density from the metal atom to the antibonding orbital of the π-allyl system.

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CONCLUSIONS

1. By the technique of matrix isolation of products from the vacuum pyrolysis of 1,5-hexadiene-d_{10}, the IR spectrum of the free allyl radical C_3D_5 has been obtained for the first time.

2. On the basis of the IR spectra of the C_3H_5 and C_3D_5 radicals, vibrational frequencies of the allyl radical have been calculated, and the bands have been assigned to the normal vibrations.

3. A systematic comparison has been made of the vibrational frequencies of the allyl radical and the π-allyl ligand in the composition of organometallic compounds. It has been established that the frequencies of out-of-plane vibrations $\rho_w(CH_2)$, $\rho_t(CH_2)$, and $\rho(CH)$ are substantially higher for the π-allyl ligand; the frequencies of vibrations taking place in the plane of the allyl fragment are little different for the two cases. A new assignment has been proposed for a number of frequencies in the spectra of π-allyl complexes.

4. The system of bonds $C\overset{\cdots}{-}C\overset{\cdots}{-}C$ for the allyl radical is characterized by relatively low frequencies of stretching vibrations and the force constant $F_{C\overset{\cdots}{-}C}$ 5.8 mdyne/Å. The values of $\nu_s(CCC)$ and $\nu_{as}(CCC)$ show that upon formation of a π-allyl complex, there is no loosening of the carbon—carbon bonds of the ligand, in contrast to π-complexes of unsaturated compounds.

LITERATURE CITED

1. S. Cradock and A. J. Hinchcliffe, Matrix Isolation, Cambridge University Press (1975).
2. A. K. Mal'tsev, R. G. Mikaélyan, and O. M. Nefedov, Dokl. Akad. Nauk SSSR, 201, 901 (1971).
3. T. A. Miller, Ann. Rev. Phys. Chem., 27, 127 (1976); L. A. Kotorlenko and S. A. Samoilenko, Usp. Khim., 46, 639 (1977).
4. S. D. Peyerimhoff and R. J. Buenker, J. Chem. Phys., 51, 2528 (1969).
5. G. B. Levin and W. A. Goddard III, J. Am. Chem. Soc., 97, 1649 (1975).
6. R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 39, 2147 (1963).
7. P. J. Krusic, P. Meakin, and B. E. Smart, J. Am. Chem. Soc., 96, 6211 (1974).
8. H. G. Korth, H. Trill, and R. Sustman, J. Am. Chem. Soc., 103, 4483 (1981).
9. F. A. Houle and J. L. Beauchamp, J. Am. Chem. Soc., 100, 3290 (1978).
10. A. K. Mal'tsev, V. A. Korolev, N. D. Kagramanov, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 1078 (1983).
11. V. T. Aleksanyan and B. V. Lokshin, "Vibrational spectra of π-complexes of transition elements," in: Summaries of Sciences and Technology (Itogi Nauki i Tekhniki), Structure and Chemical Bonding [in Russian], VINITI, Moscow (1976), Vol. 5.

12. A. K. Mal'tsev, V. A. Korolev, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 2415 (1982).
13. H. Bock, S. Mohmand, T. Hirabayashi, G. Maier, and H. P. Reisenauer, Chem. Ber., 116, 273 (1983).
14. G. Maier, H. P. Reisenauer, B. Rohde, and K. Dehnicke, Chem. Ber., 116, 732 (1983).
15. T. Takeda and M. Dupius, J. Am. Chem. Soc., 105, 1713 (1983).
16. J. H. Schachtschneider, Vibrational Analysis of Polyatomic Molecules, Technical Report 231–64, Shell Development Co., Emeryville, California (1964).
17. L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, Vibrational Spectra of Polyatomic Molecules [in Russian], Nauka, Moscow (1971).
18. G. N. Bondarenko and A. V. Kotov, Izv. Akad. Nauk SSSR, Ser. Khim., 2613 (1973).
19. L. J. Bellamy, The Infra-Red Spectra of Complex Molecules, 2nd edn., Methuen, London (1958).
20. É. N. Yurchenko, L. I. Kozhevina, and V. I. Smirnov, Zh. Prikl. Spektrosk., 23, 475 (1975).
21. H. D. Murdoch and E. Weiss, Helv. Chim. Acta, 45, 1927 (1962).
22. D. M. Adams and A. Squire, J. Chem. Soc. A, 1808 (1970).
23. K. Shobatake and K. Nakamoto, J. Am. Chem. Soc., 92, 3339 (1970).
24. C. Sourisseau and B. Pasquier, Can. J. Spectrosc., 18, 91 (1973).
25. L. J. Bellamy, Advances in Infrared Group Frequencies, Halsted, New York (1968).
26. G. N. Bondarenko, in: Research in the Field of Petroleum Chemistry [in Russian], INKhS Akad. Nauk SSSR, Moscow (1976), p. 182.
27. J. R. Durig, W. E. Bucy, L. A. Carreira, and C. J. Wurrey, J. Chem. Phys., 60, 1754 (1974).
28. J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, J. Chem. Phys., 23, 315 (1955).
29. R. J. Buenker, S. D. Peyerimhoff, and H. L. Hsu, Chem. Phys. Lett., 11, 65 (1971).
30. H. P. Fritz, Chem. Ber., 94, 1217 (1961).
31. G. Davidson and D. C. Andrews, J. Chem. Soc., Dalton Trans., 126 (1972).
32. D. C. Andrews and G. Davidson, J. Chem. Soc., Dalton Trans., 1381 (1972).
33. G. Paliani, A. Poletti, G. Cardaci, S. M. Murgia, and R. Cataliotti, J. Organomet. Chem., 60, 157 (1973).
34. G. N. Bondarenko and A. V. Kotov, Dokl. Akad. Nauk SSSR, 219, 1150 (1974).
35. L. A. Leites, V. T. Aleksanyan, and T. B. Chenskaya, Dokl. Akad. Nauk SSSR, 215, 634 (1974).
36. T. B. Chenskaya, L. A. Leites, V. T. Aleksanyan, L. S. Isaeva, and L. N. Lorens, Izv. Akad. Nauk SSSR, Ser. Khim., 2716 (1974).
37. T. B. Chenskaya, L. A. Leites, V. T. Aleksanyan, A. S. Ivanov, and A. Z. Rubezhov, Izv. Akad. Nauk SSSR, Ser. Khim., 2011 (1974).
38. L. I. Kozhevina and É. N. Yurchenko, Zh. Prikl. Spektrosk., 21, 291 (1974).
39. T. B. Chenskaya, L. A. Leites, I. I. Kritskaya, and G. M. Babakhina, Izv. Akad. Nauk SSSR, Ser. Khim., 1292 (1975).
40. D. C. Andrews and G. Davidson, J. Organomet. Chem., 124, 181 (1977).
41. B. J. Brisdon, D. A. Edwards, and J. W. White, J. Organomet. Chem., 175, 113 (1979).
42. M. J. Grogan and K. Nakamoto, J. Am. Chem. Soc., 88, 5454 (1966).
43. M. Green, Organometallic Compounds of Transition Elements [Russian translation], Mir, Moscow (1972).
44. S. F. A. Kettle and R. J. Mason, J. Organomet. Chem., 5, 576 (1966); I. I. Kritskaya, in: Methods of Heteroorganic Chemistry; Types of Organometallic Compounds of Transition Metals, Book 2 [in Russian], Nauka, Moscow (1975), pp. 751–752.
45. V. T. Aleksanyan, I. A. Garbusova, T.M. Chernyshova, Z. V. Todres, M. R. Leonov, and N. I. Gramateeva, J. Organomet. Chem., 217, 169 (1981).
46. L. Radom, P. C. Hariharan, J. A. Pople, and P. V. R. Schleyer, J. Am. Chem. Soc., 95, 6531 (1973); D. W. Boerth and A. Streitweiser, Jr., J. Am. Chem. Soc., 100, 750 (1978).
47. N. S. Baird, R. R. Gupta, and K. F. Taylor, J. Am. Chem. Soc., 101, 4531 (1979).
48. C. Sourisseau and B. Pasquier, Spectrochim. Acta A, 31, 287 (1975); C. Sourisseau, J. Mol. Struct., 112, 1973 (1979).
49. M. A. Porai-Koshits and G. A. Kukina, in: Summaries of Sciences and Technology (Itogi Nauki i Tekhniki), Crystal Chemistry [in Russian], VINITI, Moscow (1974), Vol. 10, pp. 45-63; J. W. Faller, D. A. Haitko, R. D. Adams, and D. F. Chodosh, J. Am. Chem. Soc., 101, 865 (1979); P. V. Rinze and U. Müller, Chem. Ber., 112, 1973 (1979).
50. J. J. Brooks, W. Rhine, and G. D. Stucky, J. Am. Chem. Soc., 94, 7339 (1972).
51. S. P. Gubin, A. Z. Rubezhov, and L. I. Voronchikhina, J. Organomet. Chem., 149, 123 (1978).