# Molecular Associations between Indolizines and Tetracyanoethylene



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Spectroscopic, thermodynamic and kinetic properties of molecular interactions between indolizines and tetracyanoethylene are reported. The interactions involved in the complexes are weak as evidenced by the low formation constants. The kinetic behaviour indicates the initial formation of a π-complex that is rapidly transformed into a σ-complex and thereafter into the final adduct(s). Apart from the results obtained by other techniques, infrared data clearly evidence vibrational contributes characteristic of the complexes, the tricyanovinyl derivatives and the tetracyanoethylene radical anion.

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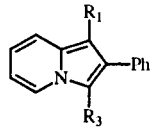
## Introduction.

Molecular complexes of nitrogen containing aromatic systems with tetracyanoethylene (TCNE) received great attention in the past decades for their mechanistic interest, because they can be considered as possible intermediates during the formation of tricyanovinyl adducts [1]. Indolizines represent an interesting class of donors, but their complexes with acceptors like TCNE are rather unstable: as a consequence, the study of molecular complexes as transient species in the tricyanovinylation of these donors, has not been attempted yet [2].

In the present work molecular associations of a representative number of indolizines (Scheme) with TCNE are investigated by studying the formation constants, the solvent effect and the kinetic behaviour.

Scheme




| | Donors | | | TCV adducts | |
|---|---|---|---|---|---|
| | $R_1$ | $R_3$ | | $R_1$ | $R_3$ |
| **1** | H | H | **14** | TCV | H |
| **2** | Ph | H | **15** | H | TCV |
| **3** | H | Ph | **16** | Ph | TCV |
| **4** | Ph | Ph | **17** | TCV | Ph |
| **5** | Me | H | **18** | Me | TCV |
| **6** | H | Me | **19** | TCV | Me |
| **7** | N=NPh | Me | | | |
| **8** | SMe | Me | | | |
| **9** | CHO | Me | | | |
| **10** | $NO_2$ | Me | | | |
| **11** | COMe | Me | | | |
| **12** | Me | CHO | | | |
| **13** | Me | COMe | | | |

## Results and Discussion.

Absorption maxima ($\lambda_{max}$) of the molecular complexes (MC) **1*-13*** and their transition energies ($E_T$) are listed in Table 1 together with the ionization potentials ($I^D$) of the donors. The $\lambda_{max}$ fall in a region where no absorptions of the donors (**D**) and the acceptors (**A**) are found. The ionization potentials $I^D$ of donors **1-13** were evaluated using the empirical equation (1) [3] and compared with the values quoted by using the equation (2) [4], (Table 1, in parenthesis):

$$I^D = 5.21 + 1.65\times10^{-4}\nu\ (cm^{-1}) \qquad (1)$$

$$I^D = 6.69 + 1.124E^{1/2}_{Ox} \qquad (2)$$

Table 1

Absorption Maxima ($\lambda_{max}$, nm), Ionization Potentials ($I^D$, eV) and Transition Energies ($E_T$, kcalmol$^{-1}$) for the complexes **1*-13*** in Dichloroethane at 25°C

| Donor | $\lambda_{max}$ | $I^D$ | [4] | $E_T$ |
|---|---|---|---|---|
| **1** | 680 | 7.64 | (7.15) | 42.10 |
| **2** | 792 | 7.29 | - | 36.15 |
| **3** | 740 | 7.44 | - | 38.70 |
| **4** | no MC | - | - | - |
| **5** | 648 | 7.60 | (7.12) | 41.50 |
| **6** | 675 | 7.65 | (7.07) | 42.40 |
| **7** | 900 | 7.04 | (6.88) | 31.80 |
| **8** | 744 | 7.43 | (7.06) | 38.50 |
| **9** | 700 | 7.57 | (7.38) | 40.90 |
| **10** | 520 | 8.38 | - | 55.10 |
| **11** | 800 | 7.27 | (7.25) | 35.80 |
| **12** | 675 | 7.65 | (7.42) | 42.40 |
| **13** | 764 | 7.37 | (7.30) | 37.50 |

From the $\lambda_{max}$ of the complexes, some considerations can be drawn: (i) comparing complexes **1*-3***, a red shift is induced by the second phenyl in the donor with an higher effect when the latter is in position 1-; in 1,2,3-triphenylindolizine **4**, some hindrance appears to prevent the formation of any complex with TCNE; (ii) a blue

shift is observed when a methyl group replaces the phenyl in position 3- (donors **3, 6**); (iii) the $I^D$ values evaluated by $\lambda_{max}$, follow an analogous trend with respect to those reported in the literature [4]; (iv) a blue shift is registered in complexes of isomeric donors **2/3, 9/12** and **11/13**, when the electron-withdrawing group is in position 3-; an opposite effect is induced in the case of an electron-releasing group (donors **5/6**).

The solvent effect was investigated for the complexes **1*-3*** by analyzing the correlations of the $\lambda_{max}$ and the transition energies $E_T$ with fε (fε is the solvent factor, $[(D-1)/(2D+1)]$ and $D$ the dielectric constant of the solvent) (Table 2). The rather small increase in $\lambda_{max}$ and $E_T$ with more polar solvents leads to no conclusion on the ground state of the complex [5].

Table 2

Absorption Maxima ($\lambda_{max}$ nm) and Transition Energies ($E_T$, kcalmol$^{-1}$) of the Complexes **1*-3*** and Solvent factor (fε) of Various Solvents at 10°C

| | | 1* | | 2* | | 3* | |
|---|---|---|---|---|---|---|---|
| Solvents | fε | $\lambda_{max}$ | ($E_T$) | $\lambda_{max}$ | ($E_T$) | $\lambda_{max}$ | ($E_T$) |
| Dioxane | 0.22 | 652 | (43.9) | 778 | (36.8) | 714 | (40.1) |
| Benzene | 0.23 | 669 | (42.7) | 784 | (36.5) | 738 | (38.8) |
| Chloroform | 0.36 | 686 | (41.7) | 800 | (35.8) | 723 | (39.6) |
| Dichloromethane | 0.42 | 660 | (43.4) | 792 | (36.1) | 716 | (40.0) |
| Dichloroethane | 0.43 | 680 | (42.1) | 792 | (36.1) | 740 | (38.7) |
| Acetonitrile | 0.48 | 688 | (41.6) | - | - | 732 | (39.1) |

Formation constants (10-20 lmol$^{-1}$) were determined for complexes **1*-3*** using both Benesi-Hildebrand ([D]>>[A]) and equimolar ([D]=[A]) methods [6,7]. From the results the systems were classified as medium strength 1:1 complexes.

The dependence of the $\lambda_{max}$ and of the formation constants from the nature and position of the substituent(s) and from the ionization potential of the donor, are in agreement with Mulliken's theory [8] and account for the formation of planar face-to-face acceptor-donor complexes. Through-space and hindrance contributes to the association, come from the substituent(s).

The formation of radical species has been evidenced by ESR determinations. On mixing the reactants, a strong TCNE radical anion signal was detected that decreased as the amount of tricyanovinyl adduct increased, therefore the molecular complex as an intermediate step in the electrophilic reaction of TCNE with indolizine can be assumed [1].

The kinetics of disappearance of the π-complex in **1*** and of the formation of the tricyanovinyl adducts **14-19** have been performed and the results compared with literature data for close systems [9]. A three-step reaction can be hypothesized: (a) the rapid formation of a π-complex, (b) the formation of a σ-complex and (c) the final formation of the tricyanovinyl derivative. Rate determinations for the decomposition of the complex **1*** indicate that the kinetics do not depend on some simple function of the indolizine concentration. In particular, as shown in Table 3, the reaction is not of first order with respect to $[D]_o$: in fact, the second order rate coefficients ($k_{exp}$ are obtained by dividing first order coefficients by indolizine concentration) increase by increasing the donor concentration. On the basis of these results, one can propose a competition between two different pathways: (1) the reaction of the molecular complex with a second molecule of indolizine and (2) the direct reaction between the free TCNE and the donor, both yielding the σ-complex:

Table 3

Pseudo First-Order Coefficients (k) and Second-Order Coefficients ($k_{exp}$) for the Decomposition of the Complex **1*** in Chloroform at 25°C ($[A]_o = 2.3x10^{-4}$)

| $[D]_o$ | k | $k_{exp}$ | k' |
|---|---|---|---|
| 0.03122 | 0.72 | 23.19 | 48.2 |
| 0.02498 | 0.50 | 20.02 | 53.3 |
| 0.01873 | 0.31 | 16.38 | 58.5 |
| 0.01249 | 0.12 | 9.37 | 41.8 |

$$k_{exp} = (k'K_f[D]_o + k'')/(1 + K_f[D]_o)$$

These results are also confirmed by the linearity of the plot of $k_{exp}/(1 + K_f[D]_o)$ vs $K_f[D]_o$.

The electrophilic attack of TCNE to donors **2, 3, 5** and **6** leads to the formation of only one tricyanovinyl derivative (**16, 17, 18** and **19**, respectively), while with donor **1** the formation of two adducts (**14, 15**) is confirmed by mass determinations and ir, $^1$H nmr spectra [2,10]. The kinetics of formation of the final products **14-19** were found to be first order with respect to the donor and the σ-complex. The rate coefficients increase with the polarity of the solvent and by adding a base like *N,N*-diethylaniline, the second result indicating that a proton is removed from the σ-complex by the indolizine [9].

On completion of the research, intra- and intermolecular charge-transfer transitions in the tricyanovinyl adducts have also been investigated either in solution or in the solid state by means of uv-vis and Ft-ir techniques. The uv-vis spectra of products **14-19** show the same trend already reported in the literature for close systems [11]. The measurements were carried out on samples in the solid state or absorbed on silica gel or in chloroform solution: in the solid state, two groups of intramolecular absorptions in the range 400-480 and 500-560 nm and a group of intermolecular bands at lower frequencies (600-

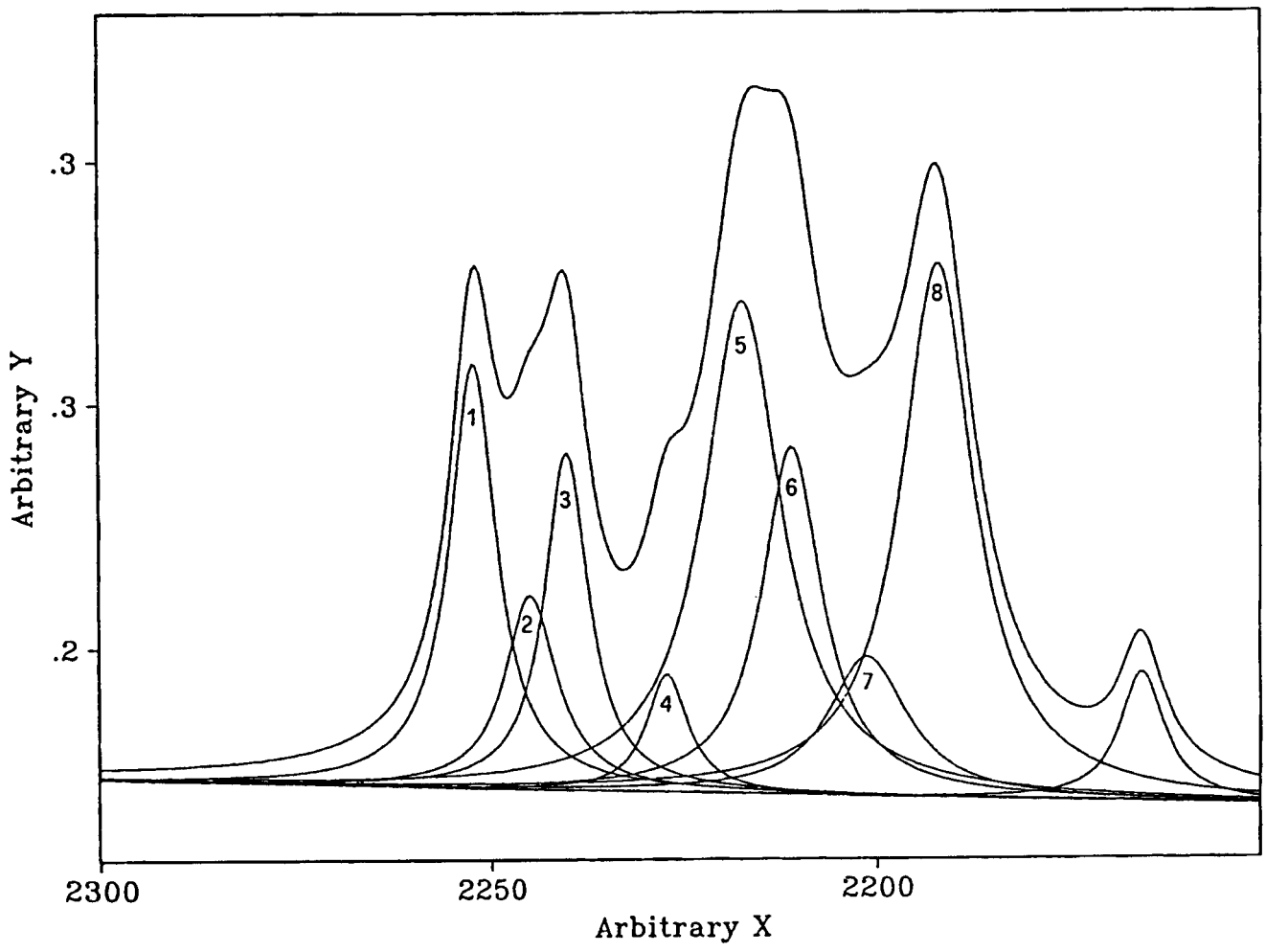



Figure 1. Band splittings for the system **6**/TCNE in the region 2300-2150 $cm^{-1}$. Assigned modes: TCNE (2252, 2245, 2217 $cm^{-1}$, peaks 1, 2 and 5), tricyanovinyl adduct (2227, 2217 $cm^{-1}$, peaks 4 and 5), complex (2240 $cm^{-1}$, peak 3), TCNE radical anion (2211, 2201, 2192 $cm^{-1}$, peaks 6, 7 and 8).

770 nm) were observed; on silica gel, only the two groups of intramolecular absorptions were present, while in chloroform solution only the group at 500-560 nm was detected. In particular, the independence of the intramolecular bands from the position of the tricyanovinyl group and from the substituent as well as the presence of additional intermolecular bands in **14, 17, 19** (due to inductive effect from the vicinal nitrogen) appear to be characteristic of the solid state.

The localization of the band of a complex by infrared spectroscopy has received scarce attention in the past mainly due to the inadequacy of the spectrometers. In a previous work on complexes of TCNE with aromatic hydrocarbons, we were able to detect the band of the complex in the region of TCNE stretching modes [12]. In this work the reaction path has been evidenced through the analysis of the TCNE modes in the region 2300-2150 $cm^{-1}$: as an example the band profile of the system **6**/TCNE is shown in Figure 1. Band splittings on the spectrum of this reaction after 10 minutes, compared with the modes of starting TCNE (2252, 2245, 2217 $cm^{-1}$, peaks 1, 2 and 5) and of the tricyanovinyl adduct (2227, 2217 $cm^{-1}$, peaks 4 and 5), show the absorptions of the complex (2240 $cm^{-1}$, peak 3) and those of the radical anion (2211, 2201, 2192 $cm^{-1}$, peaks 6, 7 and 8). These assignments are confirmed by comparison with reference spectra [13].

## EXPERIMENTAL

The uv-vis determinations in solution were carried out on a Perkin-Elmer 554 spectrophotometer equipped with a MgW-K2R thermostatting system and the temperature was kept within ± 0.1°. Solid state uv-vis spectra were recorded on the same spectrophotometer equipped with a Perkin-Elmer integrating sphere. Ft-ir measurements in solution were carried out on a Nicolet Fourier Transform Infrared 20-SX spectrophotometer using a thermostatted variable cell (pathlength 0.3 cm) with

sodium chloride plates; for solid state spectra the same spectrophotometer was equipped with a Spectra Tech. "Collector" for DRIFT measurements. Band splittings were performed using a Galactic package software, supposing a Lorentzian character. The $^1$H nmr spectra were performed on a Varian Gemini 200 (working at 199.975 MHz); the protons were assigned on the basis of the data reported in literature [2,10]. Mass spectra were recorded on a Carlo Erba QMD 1000 mass spectrometer. The esr spectra were recorded on a Varian E-4 spectrometer using a deareated two-leg inverted cell described previously [14].

All the donors were prepared according to literature [15]. Tetracyanoethylene was Aldrich RP-ACS grade reagent and was sublimed at reduced pressure (110°, 3 Torr). The solvents were Carlo Erba RP-ACS grade and were purified and dried according to the literature [16].

General Procedure for the Synthesis of the Complexes.

Equimolar solutions of donor and acceptor in dichloroethane (the most suitable solvent in a compromise between solubility of the reactants and the stability of the complexes) were mixed at room temperature and the $\lambda_{max}$ of the MC bands evaluated.

Spectrophotometric Determinations of the Formation Constants on Complexes **1*-3*** in Chloroform at 20°.

Due to low extinction coefficients and stability of the complexes, the determination of the formation constants was limited to solutions of the systems **1*-3*** in chloroform which was the most suitable solvent.

Benesi-Hildebrand Method.

The concentration dependence of the absorbance of the MC band ($d$) for a 1:1 complex is given by:

$$[A]_o/d = 1/K_f\varepsilon[D]_o + 1/\varepsilon$$

under conditions in which the total concentration of the electron donor, $[D]_o$, is in large excess relative to the total concentration of the acceptor, $[A]_o$, and for a 1 cm light path. $K_f$ is the formation constant and $\varepsilon$ is the molar extinction coefficient of the complex at the monitoring wavelength. Plots of $[A]_o/d$ against $1/[D]_o$ for solutions in which $[D]_o >> [A]_o$ should be linear [6].

As an example of a standard procedure, uv-vis measurements for the complex **1*** are reported. From freshly prepared stock solutions of indolizine **1**, approximately 0.014 *M*, and of TCNE, approximately 7 x $10^{-4}$ *M*, eight samples were prepared by mixing 0.40, 0.60, 0.80, 1.00, 1.25, 1.50, 1.75, 2.00 cm$^3$ of donor solution and 1.00 cm$^3$ of TCNE solution; the final volume was always 3.00 cm$^3$. Five different samples of each mixture were prepared for a total of 40, on which the determinations of the absorbance ($d$) at the $\lambda_{max}$ of the complex were performed. A linear correlation was obtained by plotting $[A]_o/d$ against $1/[D]_o$, with a correlation coefficient greater than 0.999.

Equimolar Method.

If $[D]_o=[A]_o$, for a 1 cm light path,

$$K_f = d/\varepsilon([A]_o - d/\varepsilon)^2$$

hence

$$[A]_o/d^{1/2} = d^{1/2}/\varepsilon + 1/(K_f\varepsilon)^{1/2}$$

and a plot of $[A]_o/d^{1/2}$ against $d^{1/2}$ should give a straight line [7].

As an example of a standard procedure, uv-vis measurements for the complex **1*** are reported. From freshly prepared stock solutions of indolizine **1** and of TCNE, both approximately 6 x $10^{-3}$ *M*, eleven samples were prepared by mixing 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, 1.10, 1.20, 1.30, 1.40, 1.50 cm$^3$ of donor and of acceptor solutions; the final volume was always 3.00 cm$^3$. Five different samples of each mixture were prepared for a total of 55, on which the determinations of the absorbance ($d$) at the $\lambda_{max}$ of the complex were performed. A linear correlation was obtained by plotting $[A]_o/d^{1/2}$ against $d^{1/2}$, with a correlation coefficient greater than 0.999.

Synthesis of the Tricyanovinyl Derivatives **14-19.**

Satured solutions of donor and acceptor in *N,N*-dimethylformamide were mixed at room temperature under stirring. The reaction mixtures were let to react for 24 hours: a dark precipitate was collected and chromatographed on a silica gel column, using as eluant cyclohexane/ethyl acetate with a ratio from 8:2 to 1:1. The analytical and spectroscopic data of all the tricyanovinyl derivatives are reported below.

1-Tricyanovinyl-2-phenylindolizine (**14**).

This compound had mp 210-212°; uv-vis (chloroform solution): $\lambda_{max}$ 515 nm, $\varepsilon$ = 13829 lmol-1 cm$^{-1}$; ir: $\nu_{max}$ 2220.1, 2211.4 cm$^{-1}$; $^1$H nmr (deuterochloroform, which was used as reference peak, $\delta$ = 7.26 ppm): $\delta$ 7.09 (1H, td, H-6, $J_t$ = 6.7 Hz, $J_d$ = 1.1 Hz), 7.38 (2H, m, arom), 7.50 (5H, m, H-3, H-7, arom), 7.77 (1H, d, H-8, J = 9.2 Hz), 8.20 (1H, dt, H-5, $J_d$ = 6.7 Hz, $J_t$ = 1.1 Hz); ms: (m/z) 294 (M$^+$, 83.8%), 267 (50.2), 231 (52.8), 217 (45.7), 192 (87.4), 191 (100.0), 77 (72.1).

*Anal.* Calcd. for $C_{19}H_{10}N_4$: C, 77.52; H, 3.43; N, 19.05. Found: C, 77.64; H, 3.39; N, 18.97.

3-Tricyanovinyl-2-phenylindolizine (**15**).

This compound had mp 206-208°; uv-vis (chloroform solution): $\lambda_{max}$ 552 nm, $\varepsilon$ = 9440 lmol-1 cm$^{-1}$; ir: $\nu_{max}$ 2223.5, 2214.3 cm$^{-1}$; $^1$H nmr (deuterochloroform, which was used as reference peak, $\delta$ = 7.26 ppm): $\delta$ 6.85 (1H, s, H-1), 7.19 (1H, td, H-6, $J_t$ = 6.7 Hz, $J_d$ = 1.1 Hz), 7.40 (2H, m, arom), 7.50 (4H, m, H-7, arom), 7.67 (1H, d, H-8, J = 9.2 Hz), 8.30 (1H, dt, H-5, $J_d$ = 6.7 Hz, $J_t$ = 1.1 Hz); ms: (m/z) 294 (M$^+$, 100.0%), 267 (59.3), 217 (15.1), 191 (18.5), 77 (37.9).

*Anal.* Calcd. for $C_{19}H_{10}N_4$: C, 77.52; H, 3.43; N, 19.05. Found: C, 77.60; H, 3.39; N, 19.01.

3-Tricyanovinyl-1,2-diphenylindolizine (**16**).

This compound had mp 226-228°; uv-vis (chloroform solution): $\lambda_{max}$ 532 nm, $\varepsilon$ = 17292 lmol-1 cm$^{-1}$; ir: $\nu_{max}$ 2222.0, 2214.3 cm$^{-1}$; $^1$H nmr (deuterochloroform, which was used as reference peak, $\delta$ = 7.26 ppm): $\delta$ 7.02 (1H, td, H-6, $J_t$ = 6.7 Hz, $J_d$ = 1.1 Hz), 7.15 (2H, m, arom), 7.33 (5H, m, arom), 7.50 (4H, m, arom), 7.73 (1H, d, H-8, J = 9.2 Hz), 8.16 (1H, dt, H-5, $J_d$ = 6.7 Hz, $J_t$ =1.1 Hz); ms: (m/z) 370 (M$^+$, 100.0%), 343 (22.5), 316 (15.8), 267 (25.3), 77 (25.4).

*Anal.* Calcd. for $C_{25}H_{14}N_4$: C, 81.06; H, 3.81; N, 15.13. Found: C, 81.17; H, 3.77; N, 15.06.

1-Tricyanovinyl-2,3-diphenylindolizine (**17**).

This compound had mp 147-150°; uv-vis (chloroform solution): $\lambda_{max}$ 544 nm, $\varepsilon$ = 15276 lmol-1 cm$^{-1}$; ir: $\nu_{max}$ 2222.5, 2213.8 cm$^{-1}$; $^1$H nmr (deuterochloroform, which was used as

reference peak, δ = 7.26 ppm): δ 7.30 (12H, m, H-6, H-7, arom), 7.74 (1H, d, H-8, J = 9.0 Hz), 8.20 (1H, dt, H-5, $J_d$ = 6.8 Hz, $J_t$ = 1.1 Hz); ms: (m/z) 370 ($M^+$, 33.8%), 341 (56.3), 314 (18.5), 267 (22.8), 191 (100.0), 77 (31.6).

*Anal.* Calcd. for $C_{25}H_{14}N_4$: C, 81.06; H, 3.81; N, 15.13. Found: C, 80.98; H, 3.83; N, 15.19.

3-Tricyanovinyl-1-methyl-2-phenylindolizine (**18**).

This compound had mp 214-215°; uv-vis (chloroform solution): $\lambda_{max}$ 532 nm, ε = 15851 lmol-1 $cm^{-1}$; ir: $\nu_{max}$ 2226.0, 2209.8 $cm^{-1}$; $^1H$ nmr (deuterochloroforrn, which was used as reference peak, δ = 7.26 ppm): δ 2.40 (3H, s, $CH_3$), 7.25 (1H, td, H-6, $J_t$ = 7.0 Hz, $J_d$ = 1.4 Hz), 7.30 (2H, m, arom), 7.52 (4H, m, H-7, arom), 7.68 (1H, dt, H-8, $J_d$ = 8.7 Hz, $J_t$ = 1.2 Hz), 8.15 (1H, dt, H-5, $J_d$ = 7.0 Hz, $J_t$ = 1.0 Hz); ms: (m/z) 308 ($M^+$, 67.4%), 293 (32.9), 281 (79.5), 231 (25.7), 192 (100.0), 77 (15.2).

*Anal.* Calcd. for $C_{20}H_{12}N_4$: C, 77.91; H, 3.92; N, 18.17. Found: C, 77.85; H, 3.95; N, 18.20.

1-Tricyanovinyl-2-phenyl-3-methylindolizine (**19**).

This compound had mp 197-199°; uv-vis (chloroform solution): $\lambda_{max}$ 528 nm, ε = 14301 lmol-1 $cm^{-1}$; ir: $\nu_{max}$ 2222.2, 2211.3 $cm^{-1}$; $^1H$ nmr (deuterochloroform, which was used as reference peak, δ = 7.26 ppm): δ 2.49 (3H, s, $CH_3$), 7.20 (1H, td, H-6, $J_t$ = 7.0 Hz, $J_d$ = 1.4 Hz), 7.30 (2H, m, arom), 7.50 (4H, m, H-7, arom), 7.75 (1H, dt, H-8, $J_d$ = 8.7 Hz, $J_t$ = 1.2 Hz), 8.10 (1H, dt, H-5, $J_d$ = 7.0 Hz, $J_t$ = 1.0 Hz); ms: (m/z) 308 ($M^+$, 48.2%), 293 (15.9), 281 (52.7), 231 (67.3), 192 (100.0), 77 (45.7).

*Anal.* Calcd. for $C_{20}H_{12}N_4$: C, 77.91; H, 3.92; N, 18.17. Found: C, 77.80; H, 3.94; N, 18.26.

Kinetic Procedure for the Decomposition of **1***.

From freshly prepared stock chloroform solutions of indolizine **1** (from 1.2 x $10^{-2}$ to 3.2 x $10^{-2}$ *M*) and of TCNE (approximately 2.3 x $10^{-4}$ *M*) four different samples, obtained varying the indolizine concentration, were prepared, on which the decrease in absorbance at the $\lambda_{max}$ of the complex was measured. The temperature was kept constant at 25° and the initial time was taken when the reactants were mixed. The experimental data were treated by using an appropriate software package.

Kinetic Procedure for the Formation of **14-19**.

The measurements were carried out in various solvents, like chloroform, acetonitrile and *N,N*-dimethylformamide; in all cases the reaction was very slow compared with the decomposition of the π-complex and the yields resulted lower than 35%. As standard procedure, the formation of the tricyanovinyl derivative **14** is reported. Equimolar stock chloroform solutions of indolizinc **1** and of TCNE, approximately 1.89 x $10^{-3}$ *M*, freshly prepared, were mixed and the increase in absorbance at the $\lambda_{max}$ of the product was measured. The temperature was kept constant at 25° and the initial time was taken when the reactants were mixed. To confirm the proposed mechanism, in the case of **14**, catalytic amounts of *N,N*-diethylaniline were added to the reactants. The experimental data were treated by using an appropriate software package.

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