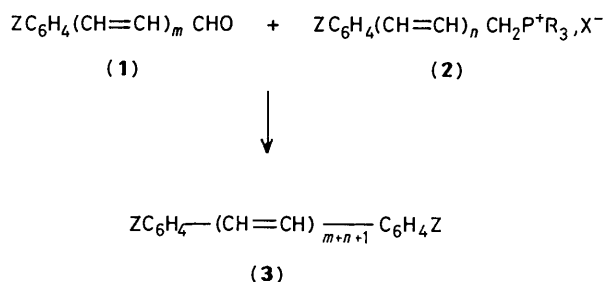# Preparation of p,p'-Disubstituted-α,ω-Diphenyl Polyenes

Charles W. Spangler,* Ray K. McCoy, Alexa A. Dembek, Linda S. Sapochak, and Bradley D. Gates
The Michael Faraday Laboratories, Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115 U.S.A.

Condensation of appropriately substituted benzaldehydes or cinnamaldehydes with either bis-Wittig reagents or bis-phosphonate esters (Horner-Emmons-Wadsworth modifications) containing one or two double bond units are general and quite efficient preparations of functionalized α,ω-diphenyl-polyenes containing 3, 4, 5, or 6 conjugated double bonds having all-*E* configurations. Bis-Wittig reagents prepared from tributyl rather than the more normally utilized triphenylphosphine are much more reactive, particularly for bis-condensations in which the benzaldehyde or cinnamaldehyde is substituted with electron-donating groups.
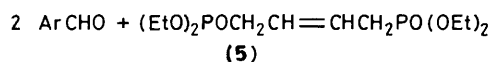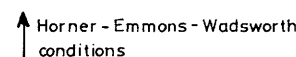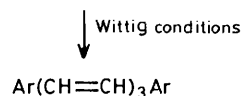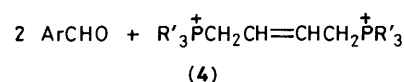
The synthesis of conjugated polyenes has been of continuing interest over the years, particularly for modelling the spectroscopic behaviour of extended conjugated systems.[1] Recently, various spectroscopic investigations of both pristine and chemically doped polymers such as polyacetylene have been used to attempt to analyse the chemical nature of dopant–polymer interaction.[2] This has led to a rather wide-ranging and continuing discussion of the nature of the charge carriers (solitons, polarons, and bipolarons), and the relative roles of interchain *versus* intrachain charge transport.[3,4] Most recently, it has been recognized that conjugated electroactive polymers may also have significant nonlinear optical (NLO) activity,[5] and that, in particular, the third order susceptibility, $\chi^{(3)}$, is influenced by π-electron delocalization. DeMelo and Silbey[6] have recently considered the effect of increasing delocalization and its effect on nonlinear polarizabilities for regular polyenes, solitons, polarons, and bipolarons, and they have suggested that polyenes containing strongly polar substituent groups may have greatly enhanced hyperpolarizabilities. Thus, since NLO activity is intrinsically electronic in nature, the availability of polyenes of various chain lengths with highly polar groups may catalyse further study in this area, with the real possibility that electro-optic devices depending on the fast switching times normally associated with polyene spectroscopy can be built using organic nonlinear materials.

α,ω-Diphenylpolyenes are ideally suited as potential organic nonlinear optical materials since they are thermally stable and not prone to the facile isomerization or polymerization seen in the parent alkapolyene series. One can readily envision such a series of diphenyl polyenes being prepared by standard Wittig methodology and in fact, several diphenylhexatrienes have been prepared in this fashion.

$$ZC_6H_4(CH{=}CH)_m\,CHO \quad + \quad Z\,C_6H_4(CH{=}CH)_n\,CH_2P^+R_3\,,X^-$$

$$(1) \qquad\qquad\qquad (2)$$

$$ZC_6H_4{-}(CH{=}CH)\underset{m+n+1}{}C_6H_4Z$$

$$(3)$$

Z, Z = alkyl, NO_2, MeO, Me_2N, H
R = C_6H_5; X = Cl or Br; m, n = 0,1,2

The desirability of this approach becomes much less attractive for substituted diphenylpolyenes in which $m + n + 1$ is greater than 3 owing to the general unavailability of substituted phenylpolyenals containing more than one double bond. Even when available, the assembly of the two halves of the Wittig reaction pair is at best tedious. A much more efficient approach[8] has been described by several workers for the synthesis of symmetrically substituted diphenylpolyenes utilizing bisphosphoranes:

$$2\ ArCHO \;+\; R'_3\overset{+}{P}CH_2CH{=}CHCH_2\overset{+}{P}R'_3$$

$$(4)$$

↓ Wittig conditions

$$Ar(CH{=}CH)_3Ar$$

↑ Horner-Emmons-Wadsworth conditions

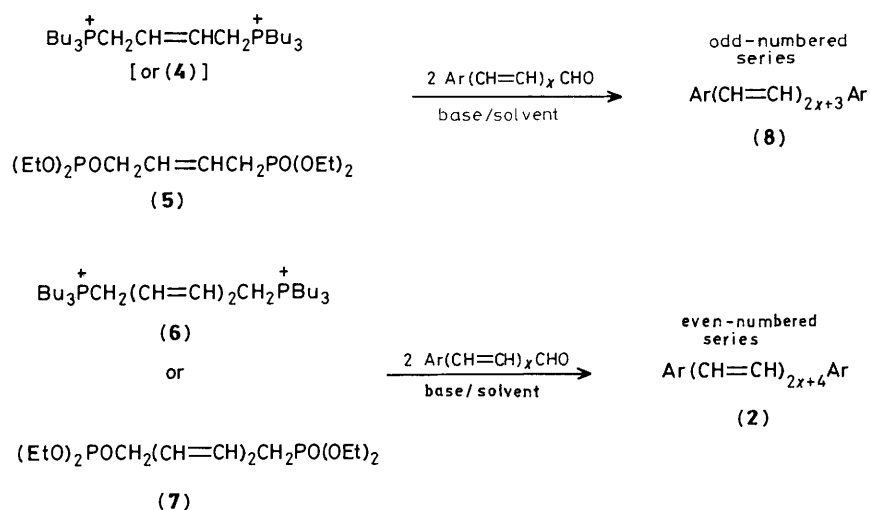$$2\ ArCHO \;+\; (EtO)_2POCH_2CH{=}CHCH_2PO(OEt)_2$$

$$(5)$$

However, very few polyenes containing more than three double bonds have been prepared by either method, except for the parent diphenylpentaene,[8b] especially those containing an even number of double bonds which cannot be obtained from either of the above bisphosphoranes.
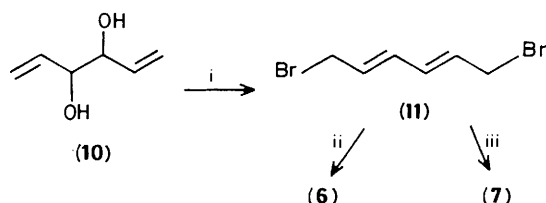
We now report that bisphosphoranes are extremely useful *general* reagents for the preparation of symmetrically substituted diphenylpolyenes, either by Wittig (W) or Horner-Emmons-Wadsworth (HEW) approaches.

All of the condensations can be carried out quite readily at room temperature with NaOEt–EtOH or DMF being used for Wittig reactions and KOBuᵗ–glyme for HEW modifications. In each case the all-*E* isomer crystallizes directly from solution. Thus, substituted benzaldehydes give the triene and octatetraene series, while substituted cinnamaldehydes yield pentaenes and hexaenes in reasonably good yields (30—80%), considering that no attempts have been made to optimize individual reactions. These results are summarized in the Table.

Although the bis-Wittig salt (4) and the bisphosphonate ester (5) have been utilized in polyene synthesis previously, usually producing various disubstituted diphenylhexatrienes, the dienyl counterparts (6) and (7) needed to prepare polyenes containing an even number of conjugated links were previously unknown.

$Bu_3\overset{+}{P}CH_2CH{=}CHCH_2\overset{+}{P}Bu_3$

[or (**4**)]

$\xrightarrow[\text{base/solvent}]{\text{2 Ar(CH=CH)}_x\text{CHO}}$

odd-numbered series

$Ar(CH{=}CH)_{2x+3}Ar$

(**8**)

$(EtO)_2POCH_2CH{=}CHCH_2PO(OEt)_2$

(**5**)

$Bu_3\overset{+}{P}CH_2(CH{=}CH)_2CH_2\overset{+}{P}Bu_3$

(**6**)

or

$\xrightarrow[\text{base/solvent}]{\text{2 Ar(CH=CH)}_x\text{CHO}}$

even-numbered series

$Ar(CH{=}CH)_{2x+4}Ar$

(**2**)

$(EtO)_2POCH_2(CH{=}CH)_2CH_2PO(OEt)_2$

(**7**)

Both can be prepared from E,E-1,6-dibromohexa-2,4-diene in good yield:

Wittig condensation (or the corresponding HEW modification) was effected by dropwise addition of a solution of base to a stoicheiometric (2:1) mixture of the aldehyde and phosphorus reagent dissolved in a suitable solvent. Precipitation of crystalline all-E polyene commenced almost immediately, thus allowing easy isolation of the product.

There seems to be no practical limitation to the extension of these reactions to other substituent groups, assuming that appropriate substituted benzaldehydes, cinnamaldehydes, or higher phenylpolyenals are available, and that a suitable solvent can be found to keep the mono-reacted intermediate in solution long enough to effect the second condensation step.

We have previously reported [10] that oxidative doping of the parent members of the pentaene and hexaene series can be accomplished with either $FeCl_3$ or $SbCl_5$, but not I_2. This has been interpreted in terms of successive one-electron transfers involving formation of an intermediary polaron, followed by the more stable bipolaron state, which has recently been confirmed by e.s.r. measurements.[11] More recently we have found that electron-donating substituents (Me_2N and MeO) greatly stabilize the bipolaron states in the bis-substituted pentaenes and hexaenes, and that polaron and bipolaron formation and interconversion can be followed readily by u.v.–visible–n.i.r. spectroscopy.[12]

We anticipate that the availability of extended polyene series with strong donor or acceptor groups will further catalyse spectroscopic studies of these new materials, and that evaluations of their potential for nonlinear optical behaviour will point the way for the future design of new electro-optic devices capable of functioning at the molecular level.

Experimental

M.p.s were obtained with a Melt Temp apparatus and are uncorrected. C, H, N, Analyses were carried out in our laboratory with a Perkin-Elmer Model 240 analyser by

Table. p,p'-Disubstituted α,ω-diphenylpolyenes

$p\text{-}ZC_6H_4(CH{=}CH)_nC_6H_4Z\text{-}p$

Compd.	Z	n	Method	% Yield	M.p.^{a}
(**12**)	Me_2N	3	W	21	238—240
			HEW	47	($CHCl_3$)
(**13**)	Me_2N	4	W	37	258—260
			HEW	62	(PhMe)
(**14**)	Me_2N	5	W	60	275—276
			HEW	15	(PhMe–DMF)
(**15**)	Me_2N	6	W	69	278—280
			HEW	75	(DMF)
(**16**)	MeO	3	W	20	250—251
			HEW	34	(PhMe)^b
(**17**)	MeO	4	W	17	266—267^c
			HEW	41	(PhMe–DMF)
(**18**)	MeO	5	W	12	276—278^d
			HEW	25	(DMF)
(**19**)	MeO	6	W	38	284—285
			HEW	53	(DMF)
(**20**)	NO_2	3	W		230—231
			HEW	66	(DMF)
(**21**)	NO_2	4	W	60	246—247
			HEW	37	(DMF)
(**22**)	NO_2	5	W	64	234—236
			HEW	Low	(DMF)
(**23**)	NO_2	6	W	42	226—228
			HEW	Low	(DMF)
(**24**)	Cl	3	W	V. low	216—218
			HEW	40	(PhMe)
(**25**)	Cl	4	W	V. low	244—246
			HEW	61	(PhMe)
(**26**)	Cl	5	W	43	260—262
			HEW	9	(PhMe–DMF)
(**27**)	Cl	6	W	36	276—278
			HEW	V. low	(DMF)

W Conditions: NaOEt, 25 °C/EtOH or DMF, 16 h; HEW conditions: $KOBu^i$, 25 °C, glyme, 16 h.

^{a} Recrystallization solvent(s) in brackets. ^{b} Lit.,^{9} 247—248 °C. ^{c} Lit.,^{9} 266—267 °C. ^{d} Lit.,^{9} 276—278 °C.

Paulanne Rider. U.v.–visible spectra were recorded with a Varian Model 2290 spectrophotometer as DMF or CH_2Cl_2 solutions. ^1H N.m.r. spectra were determined as solutions in $CDCl_3$ (Me_4Si internal reference) on an IBM WP-200 spectrometer. In general, no solvent was found that yielded solutions concentrated enough to obtain ^1H n.m.r. spectra for the pentaene and hexaene series. p-Chlorobenzaldehyde,

p-methoxybenzaldehyde, *p*-nitrobenzaldehyde, and *p*-*N*,*N*-dimethylaminocinnamaldehyde were obtained from either Aldrich or Lancaster Chemical Co.

(E,E)-1,6-*Dibromohexa*-2,4-*diene* (**11**).—A solution of hexa-1,6-diene-3,4-diol[13] (149.6 g, 1.31 mol) in anhydrous ether (500 ml) was added dropwise to phosphorus tribromide (224 g, 0.90 mol) (excess) in an ice-bath cooled 1-l round-bottomed flask equipped with a dropping funnel and magnetic stirrer. After the addition was complete, the mixture was allowed to warm to room temperature and was then set aside overnight. It was then poured slowly with stirring into ice–water, and the resulting mixture neutralized by careful addition of saturated aqueous sodium carbonate. The product was extracted with ether (3 × 400 ml) and the combined extracts were washed with saturated brine (2 × 250 ml) and dried (MgSO$_4$) whilst being refrigerated. The mixture was filtered and evaporated under reduced pressure to yield the crude crystalline dibromide (263 g, 87%). A small portion of the product (which is a *potent lacrymator* and should be handled in a fume hood) was recrystallized from ether; it had m.p. 85—86 °C; δ_H 4.0—4.2 (4 H, d, *J* 7 Hz, BrCH$_2$), 5.8—6.1 (2 H, m, vinyl), 6.2—6.4 (2 H, m, vinyl) (Found: C, 30.15; H, 3.4. Calc. for C$_6$H$_8$Br$_2$: C, 30.00; H, 3.33%). The bulk of the crude dibromide could be utilized directly to form the bis-phosphorus reagents.

(E,E)-*Hexa*-2,4-*diene*-1,6-*diylbis*(*tributylphosphonium*) *Dibromide* (**6**).—1,6-Dibromohexa-2,4-diene (180 g, 0.75 mol) was weighed rapidly (hood!) and dissolved in dry toluene (1 ml) in a 2-l round-bottomed flask. Tributylphosphine (303.5 g, 1.50 mol) was added rapidly from an addition funnel with mechanical stirring. The resulting mixture was rapidly stirred overnight at room temperature after which the phosphonium salt was filtered off, washed several times with fresh toluene to remove traces of unchanged tributylphosphine, and air-dried (376 g, 78%); δ_H 1.0 (18 H, t, *J* 7 Hz, CH$_3$), 1.5 (24 H, m, CH$_2$), 2.4 (12 H, m, CH$_2$P), 3.8 (4 H, m, =C*H*CH$_2$P), 5.7 (2 H, m, vinyl), and 6.7 (2 H, m, vinyl); δ_C 13.35, 18.60, 19.55, 23.73, 24.01, 120.06, and 137.31.

(E,E)-*Tetraethyl Hexa*-2,4-*diene*-1,6-*bis*(*phosphonate*) (**7**).—Crude (*E*,*E*)-1,6-dibromohexa-2,4-diene (260 g, 0.90 mol) was dissolved in toluene (500 ml) and triethyl phosphite (415 g, 10% excess based on double reaction) was added all at once; the resulting mixture was then refluxed overnight. Solvent and excess of triethyl phosphite were removed under reduced pressure to yield crude (**7**) as a pale yellow liquid (334 g, 83%). Attempts at distillation *in vacuo* of this viscous product led to extensive decomposition and polymerization. The crude product was, therefore, used without further purification and stored at 0 °C, n_D^{25} 1.4858, δ_H 1.35 (12 H, t, *J* 7 Hz, CH$_3$), 2.5—2.8 (dd, J_{ab} 10 Hz, J_{bc} 4 Hz, CH$_2$C=C), 4.0—4.3 (m, 8 H, CH$_2$), 5.5—5.8 (m, 2 H, vinyl), and 6.1—6.4 (m, 2 H, vinyl).

General Wittig Procedure (*W*).—A *para*-substituted benz-aldehyde or cinnamaldehyde (0.02 mol) was mixed with either (*E*)-but-2-ene-1,4-diylbis(tributylphosphonium) dichloride[8e] (0.01 mol) (for the preparation of trienes or tetraenes) or (*E*,*E*)-hexa-2,4-diene-1,6-diylbis(tributylphosphonium) dibro-mide (0.01 mol) (for the preparation of pentaenes or hexaenes) in either absolute alcohol or alcohol–DMF (200 ml) depending on aldehyde solubility. A solution of sodium ethoxide in alcohol (1M; 30 ml, 0.03 mol) was added dropwise with magnetic stirring to give the onset of product precipitation generally within 5 min. After the addition was complete, the mixture was stirred overnight, and then heated for 1 h at 90 °C (oil-bath). After cooling, the product was filtered off and recrystallized from an appropriate solvent combination.

General Horner–Emmons–Wadsworth Procedure (*HEW*).—A *para*-substituted benzaldehyde or cinnamaldehyde (0.02 mol) was mixed with either (*E*)-tetraethyl (but-2-ene)-1,4-diphos-phonate[8a] (0.01 mol) (for the preparation of trienes or tetraenes) or (*E*,*E*)-tetraethyl(hexa-2,4-diene)-1,6-diphosphon-ate (0.01 mol) (for the preparation of pentaenes or hexaenes) in glyme (200 ml). A solution of potassium t-butoxide [0.03 mol in glyme (200 ml)] was added dropwise to give an exothermic reaction whose temperature can be maintained below reflux by controlling the rate of addition. After the addition was complete the mixture was stirred overnight at room temperature and then heated for 1 h at 90 °C (oil-bath). Water was then added (200—500 ml) to precipitate the product which was filtered off and recrystallized from an appropriate solvent combination. The following compounds were so prepared. 1,6-Bis(*p*-*N*,*N*-dimethylaminophenyl)hexa-1,3,5-triene (**12**); δ_H 3.0 (6 H, s, NMe$_2$), 6.4—6.8 (6 H, m, vinyl), and 7.2—7.4 (8 H, m, ArH); $\lambda_{max.}$(DMF) 410 nm ($\varepsilon_{max.}$ 46 200) (Found: C, 82.8; H, 8.0; N, 8.65. Calc. for C$_{22}$H$_{26}$N$_2$: C, 83.00; H, 8.19; H, 8.80%).

1,8-Bis(*p*-*N*,*N*-dimethylaminophenyl)octa-1,3,5,7-tetraene (**13**); δ_H 2.90 (6 H, s, NMe$_2$), 6.3—6.8 (8 H, m, vinyl), and 7.2—7.4 (8 H, m, ArH); $\lambda_{max.}$ 425 nm (68 500) (Found: C, 83.95; H, 8.05; N, 8.35. Calc. for C$_{24}$H$_{28}$N$_2$: C, 83.67; H, 8.19; N, 8.13%).

1,10-Bis(*p*-*N*,*N*-dimethylaminophenyl)deca-1,3,5,7,9-pentaene (**14**); $\lambda_{max.}$(CH$_2$Cl$_2$) 445 nm (61 000) and 470sh (Found: C, 84.05; H, 8.25; N, 7.65. Calc. for C$_{26}$H$_{30}$N$_2$: C, 84.28; H, 8.16; N, 7.56%).

1,12-Bis(*p*-*N*,*N*-dimethylaminophenyl)dodeca-1,3,5,7,9,11-hexaene (**15**); $\lambda_{max.}$(CH$_2$Cl$_2$) 458 nm (46 000) and 485sh (Found: C, 84.65; H, 8.15; N, 6.9. Calc. for C$_{28}$H$_{32}$N$_2$: C, 84.80; H, 8.13; N, 7.06%).

1,6-Bis(*p*-methoxyphenyl)hexa-1,3,5-triene (**16**); $\lambda_{max.}$(DMF) 382sh, 363 (63 000), and 348sh; δ_H 3.75 (6 H, s, OCH$_3$), 6.3—6.7 (6 H, m, vinyl), 6.81 (4 H, d, *J* 8 Hz, β-Ph), and 7.3 (4 H, d, *J* 8 Hz, α-Ph).

1,8-Bis(*p*-Methoxyphenyl)octa-1,3,5,7-tetraene (**17**); $\lambda_{max.}$(DMF) 413 nm (54 000), 390 (66 000), 370 (48 000), and 350sh.

1,10-Bis(*p*-methoxyphenyl)deca-1,3,5,7,9-pentaene (**18**); $\lambda_{max.}$(CH$_2$Cl$_2$) 435 nm (38 000), 410 (41 000), 388 (28 000), and 367sh.

1,12-Bis(*p*-methoxyphenyl)dodeca-1,3,5,7,9,11-hexaene (**19**); $\lambda_{max.}$(CH$_2$Cl$_2$) 452 nm (21 000), 426 (24 000), 402 (18 000), and 380sh (Found: C, 84.05; H, 6.95. Calc. for C$_{26}$H$_{26}$O$_2$: C, 84.28; H, 7.07%).

1,6-Bis(*p*-nitrophenyl)hexa-1,3,5-triene (**20**), in its original form had a m.p. in agreement with the literature[8e] value (218—219 °C), but apparently was obtained in different crystal form from DMF; $\lambda_{max.}$(DMF) 420 nm (56 000); δ_H 6.4—7.2 (6 H, m, vinyl), 7.5—7.7 (4 H, m, β-ring), and 8.2—8.4 (4 H, m, α-ring).

1,8-Bis(*p*-nitrophenyl)octa-1,3,5,7-tetraene (**21**); $\lambda_{max.}$(DMF) 440 nm (66 000); δ_H 6.4—6.7 (4 H, m, vinyl), 6.9—7.1 (4 H, m, vinyl), 7.5 (4 H, d, *J* 12 Hz, β-phenyl), 8.15 (4 H, d, *J* 12 Hz, α-phenyl) (Found: C, 71.1; H, 4.85; N, 7.5. Calc. for C$_{20}$H$_{16}$N$_2$O$_4$: C, 68.95; H, 4.63; N, 8.04%).

1,10-Bis(*p*-nitrophenyl)deca-1,3,5,7,9-pentaene (**22**); $\lambda_{max.}$(CH$_2$Cl$_2$) 450 nm (59 000) (Found: C, 71.1; H, 4.85; N, 7.50. Calc. for C$_{22}$H$_{18}$N$_2$O$_4$: C, 70.58; H, 5.13; N, 7.48%).

1,12-Bis(*p*-nitrophenyl)dodeca-1,3,5,7,9,11-hexaene (**23**); $\lambda_{max.}$(CH$_2$Cl$_2$) 465 nm (92 000) (Found: C, 71.8; H, 5.05; N, 7.1. Calc. for C$_{24}$H$_{20}$N$_2$O$_4$: C, 71.98; H, 5.03; N, 7.00%).

1,6-Bis(*p*-chlorophenyl)hexa-1,3,5-triene (**24**); $\lambda_{max.}$(DMF) 383 nm (132 000), 362 (196 000), and 346 (164 000); δ_H 6.4—6.9 (6 H, m, vinyl), 7.2—7.5 (8 H, m, ArH) (Found: C, 71.42; H, 4.57. Calc. for C$_{18}$H$_{14}$Cl$_2$: C, 71.77; H, 4.68%).

1,8-Bis(*p*-chlorophenyl)octa-1,3,5,7-tetraene (**25**); $\lambda_{max.}$ 408 nm (77 000), 385 (92 000), 366 (65 000), and 344sh; δ_H 6.4—6.9 (8 H, m, vinyl) and 7.2—7.5 (m, 8 H, ArH) (Found: C, 73.2; H, 4.95. Calc. for C$_{20}$H$_{16}$Cl$_2$: C, 73.4; H, 4.95%).

1,10-Bis(p-chlorophenyl)deca-1,3,5,7,9-pentaene   (26); $\lambda_{max.}(CH_2Cl_2)$ 430 nm (110 000), 405 (116 000), 385 (78 000), and 365sh nm (Found: C, 74.25; H, 5.2. Calc. for $C_{22}H_{18}Cl_2$: C, 74.29; H, 5.13%).

1,12-Bis(p-chlorophenyl)dodeca-1,3,5,7,9,11-hexaene   (27); $\lambda_{max.}(CH_2Cl_2)$ 450 nm (80 000), 422 (84 000), 400 (58 200), and 380sh (Found: C, 76.1; H, 5.5. Calc. for $C_{24}H_{20}Cl_2$: C, 75.99; H, 5.31%).

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